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Influence of the Atmosphere Upon the Precision of Telescope Pointing

By Francis E. Washer and Leo W. Scott

The probable error of a single pointing (PE_s) was measured under conditions such that the effect of the air column intervening between observer and target was introduced or eliminated at will. The substantial reduction in PE_s for the air-column-eliminated method as compared with the air-column-present method showed that precision in outdoor pointing is definitely limited by the air column. Some approximate computations were made to show that the value of PE_s cannot be appreciably reduced by increasing the magnification of the telescope above 20.

I. Introduction

In the course of the work done in connection with the Range and Height Finder Project sponsored at this Bureau by the United States Army Ordnance, it became necessary to study the factors affecting the precision of telescope pointing. A range finder is essentially a double-pointing instrument, and consequently it is possible to deduce the error that may be attributed to the purely optical phase of the range finder system from the results obtained with a single telescope. The results of investigations dealing with the precision of pointing for outdoor targets [1 and 2] [1] and the effect of magnification on the precision of indoor telescope pointing [3] have already been reported. The present study is concerned mainly with showing that the column of air intervening between target and observer places a limit on the ultimate precision that can be achieved and that, furthermore, the gain in precision resulting from increasing the magnification is negligible above a magnification of approximately 20 diameters.

It must be emphasized that the term "pointing," as used in this paper, refers to a type of pointing where all mechanical errors have been eliminated, and the error of pointing found is an attribute of the combination of the optical system, the observer, and the air column intervening between target and observer. It is wholly devoid of such errors as may result from incorrect reading of verniers and scales, such as exist on transit circles and similar mechanical devices. In addition, the term "PE_s" refers to the probable error of a single pointing about the instantaneous "true" pointing at the time at which it is made, and is a measure of the error of a single pointing determined from a number of independent pointings taken rapidly, and does not contain any appreciable effect of drift.

[1] Figures in brackets indicate the literature references at the end of this paper.

II. Method

When pointings are made on a distant outdoor target, the image-forming light moves through the intervening air and produces an image of the target in the focal plane of the objective of the viewing telescope. In bringing the image of a selected portion of the distant target into coincidence with the intersection of the cross hairs of the telescope, this setting is affected not only by the errors inherent in the combination of optical system and observer's eye but also by any error that may be contributed by the column of air intervening between telescope and target. For example, it is known that the air is at all times in a state of motion, and it is probable that this turbulence may produce small random rapidly changing deviations in the direction of the image-forming light proceeding from the target to the observer. Such deviations, if they exist, would be evidenced by a larger probable error of a single pointing for the condition of air column present than would be obtained for the same target at the same distance if the effect of air column is eliminated.

In the present experiment, a special target was used for both types of pointing. This target, a sketch of which is shown in figure 1, consisted of a frame 6 feet square with two diagonal pieces intersecting to simulate a cross hair when viewed from a great distance. The frame was provided with an arm pivoted at the top and capable of being swung

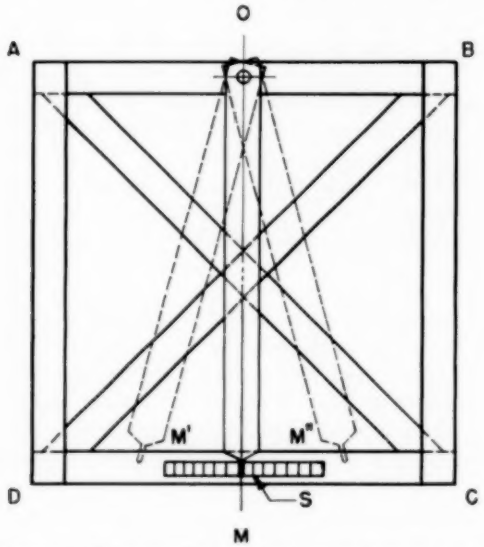

FIGURE 1. *Diagrammatic sketch of special target placed on the tower of Old Soldiers Home.*

Intersection of diagonals AC and BD form a cross. The swinging arm, OM, pivoted at O, is moved to position M' or M'' and then moved into coincidence with the center of the cross under direction of the observer stationed on the grounds of the National Bureau of Standards, distant 4,710 m. Successive settings are read with the scale, S.

from one side to the other of the intersection of the diagonal pieces. This target was placed in the tower of the Old Soldiers Home and viewed from a station on the grounds of the National Bureau of Standards. The distance separating target and observer is 4,710 meters.

1. Determination of Pointing Error When Effect of Air Column Is Present

The vertical member BC of the special target, shown in figure 1, was used as the target in the determination of pointing error with air column present. In this part of the experiment, the apparatus consisted of a telescope equipped with cross hairs and a means by which the observer could vary the pointings at the distant target without disturbing the telescope. This was accomplished by placing in front of the telescope objective a weak prism capable of rotation about its vertical axis, which is also parallel to the prism axis. As the deviation of a parallel beam of light caused by a weak prism is a function of the angle of incidence on the prism surface, the image of the target can be caused to move from side to side of the telescope cross-hair intersection by oscillating the prism. As the deviation changes slowly with the angle of incidence, this device offers a convenient means for measuring with great precision small variations in the angle of pointing. During the course of an observation the prism was rotated until the image of the target appeared to coincide with the cross hairs, and the angular position of the prism was noted with the aid of an auxiliary telescope and scale in conjunction with a mirror attached to the rotating prism. This reading was converted into seconds in the object space. A series of 10 such observations was taken and the probable error, PE_s determined from these data. Several such 10-groups are usually taken in a single run, with a short intermission between each 10-group, and the average PE_s is accepted as the value of PE_s for the run. The computation of PE_s was done in the same manner as reported in a previous paper [3].

All observations and the recording of data, in this part of the experiment, were performed by a single observer, the senior author, which together with the fact that the rotation of the prism was controlled by a smooth rod that must be released between observations, acts to reduce any effect of memory, and so tends to ensure the independence of successive observations.

2. Determination of Pointing Error When Effect of Air Column Is Eliminated

In the procedure, described in section II, 1, there can be no question but that an opportunity is afforded the intervening air column to affect the probable error of a single pointing in any manner it may. In this portion of the experiment, the same viewing telescope was used for observation, the prism was kept immovable, the distance separating target and telescope was the same, and the cross hairs in the viewing telescope were ignored. The settings were made at the target itself with the aid of a second observer, who moved the swinging arm, OM, and brought it into coincidence with the intersection of the diagonal

bars, BD, and AC in accordance with the directions of an observer at the viewing telescope. Under these conditions, the image-forming light proceeding from both the moving and fixed members of the target traversed the same column of air and was subjected to the same conditions before arrival at the viewing telescope, and it is highly improbable that these members changed their apparent relative positions with respect to one another as a result of any effect of the air column intervening between target and viewing telescope. It is true that the image of the target may move about in the focal plane of the objective of the viewing telescope, but because the image moved as a whole, and the coincidence was judged without reference to any fixed mark in the focal plane of the objective, the limit of pointing accuracy was placed by the errors inherent in the optical system, the observer's eye and ability of the second observer to move the arm, OM, in accordance with direction, and therefore any effect of the air column was reduced to a minimum. For these reasons, therefore, the effect of the air column was considered eliminated in the determination of the pointing error in this part of the experiment.

To make an observation, an observer in the tower swings the arm on its pivot sufficiently far so that the observer at the telescope can clearly see that the arm and the intersection of the diagonal bars are well separated. The arm is moved slowly to bring it toward coincidence with the intersection point, the movement being stopped when the observer at the telescope considers the moving arm and the intersection of the diagonal bars to coincide. The two observers are in constant telephonic communication throughout the course of a run. The observer in the tower records the setting with the aid of a scale placed at the bottom of the frame. A series of five such settings was made and the probable error, PE_s, computed thereupon. Several such five-groups were usually taken in a single run, with a short intermission between each five-group, and the average PE_s accepted as the value of PE_s for the run. Several runs were made for each magnification. The observer at the telescope was the same in both parts of the experiment, so any errors that may arise as a result of eye difference between observers was minimized. At the target distance selected, a movement of 1 mm at the bottom of the target frame corresponded to an angular displacement of the midpoint of the arm with respect to the intersection of the diagonal bars equal to 0.022 second when viewed from the station where the telescope was located.

III. Results of Measurements

In the course of this work, values of PE_s for several magnifications were obtained by each method of pointing. Table 1 lists the results of observation, and they are shown graphically in figure 2. It is noteworthy that for all values of magnification curve 1, which shows the value of PE_s with effect of air column present, lies above curve 2, which shows the values of PE_s with effect of air column eliminated. The failure of the points on curve 1 to lie on a smooth curve arises from variations in the atmospheric conditions rather than from any real tendency toward maxima and minima for definite magnifications. In the course of a few days, the spread of values of PE_s for a given magnification is as great as these apparent changes from one magnification to another.

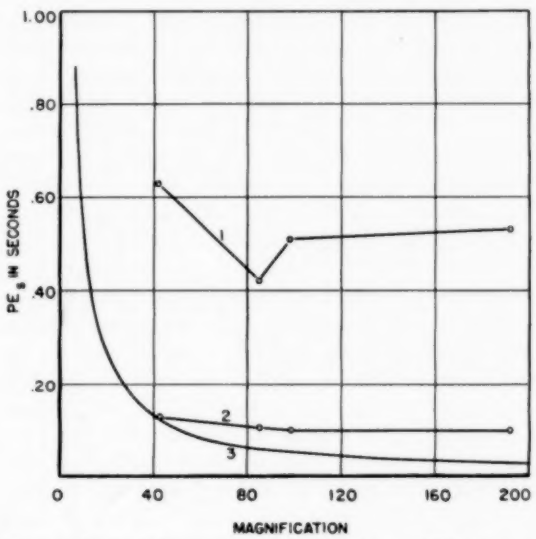

FIGURE 2. *Probable error of a single pointing (PE_s) versus magnification.*

The results are for a viewing telescope with an objective of 711-mm focal length, 100-mm aperture. Target is 4,710 m distant. Curve 1 includes the effect of air column present. For curve 2, the effect of air column is eliminated. Curve 3 is the minimum for the observer on the basis of indoor pointing.

TABLE 1.—*Probable error of a single pointing, PE_s, as a function of magnification for observations made on an outdoor target with and without the effect of air column*

Magnification	Air column eliminated			Air column present		
	PE_s	P_p	No. of 5-groups	PE_s	P_p	No. of 10-groups
	Sec.	*Sec.*		*Sec.*	*Sec.*	
42	0.12	±0.04	8	0.63	0.14	5
85	.10	.02	18	.42	.11	10
98	.09	.02	8	.51	.15	4
192	.10	.01	2	.53	.07	3

A measure of the dispersion of the values of PE_s is given in table 1, under the heading P_p. Values of P_p were obtained by considering each PE_s from a single five-group (or 10-group) as an observation and computing the probable error of a single observation from the average value of PE_s obtained for a run comprising several five-groups (or 10-groups). Where several runs are made, P_p was the average for all the runs made at a given magnification under the same conditions.

In table 2 the values of PE_s are given for observations made on the same day with the same magnifications by each method. It is noteworthy that for magnification 85, for which values are obtained on two different days, the ratio of PE_s (air column present) to PE_s (air column eliminated) is 2.9 on the first day, whereas on the second day this ratio is 5.3. It is clear that the chief cause of this change in ratio was to be found in the increase of PE_s (air column present) from 0.26 to 0.58, whereas for PE_s (air column eliminated) the change was from 0.09 to 0.11. On the first day, viewing conditions were unusually good, and this was reflected by the low values of PE_s by each method. On the second day, visibility was low and turbulence of the air caused considerable unsteadiness in the image of the target. Nevertheless, despite the low visibility, the value of PE_s (air column eliminated) increased by only 0.02 second and the value of PE_s (air column present) increased by 0.32 second.

TABLE 2.—*Comparison of PE_s for observations made on the same day with same magnification on an outdoor target with and without the effect of air column*

Magnification	Air column eliminated			Air column present			Ratio
	PE_s	P_p	No. of 5-groups	PE_s	P_p	No. of 10-groups	
	Sec	*Sec*		*Sec*	*Sec*		
42	0.13	±0.06	4	0.63	±0.14	5	4.8
85	.09	.01	8	.26	.06	5	2.9
85	.11	.02	10	.58	.16	5	5.3
192	.10	.01	2	.53	.07	3	5.3

In view of the fact that settings made by the air-column-eliminated method did not permit easy control by a single observer, it is worthwhile to consider what values of PE_s one might reasonably expect to get by this method with further refinement. Information derived from work done by the senior author on the pointing accuracy of the same telescope on an indoor target [3] was therefore used in the present study. In the course of this work nearly 10,000 observations were made and from them the following relation between the probable error (in seconds) of a single pointing and the magnification, M, of the viewing telescope was derived:

$$PE_s=\frac{4.96}{M}+0.07. \quad (1$$

It is believed that only the first term of this equation is operative in the present work, therefore values of PE_s are predicted from the relation

$$PE_s=\frac{4.96}{M}, \quad (2$$

and plotted as curve 3 in figure 2. It is clear that these values are, for the most part, appreciably lower than those plotted as curve 2. However, in view of the low values of PE_s shown in both curves 2 and 3, it is clear that little gain would result by refining the method.

Furthermore, the values of PE_s for the air-column-present method cannot be appreciably lowered by extending the number of observations. For here, too, the senior author, assisted by Helen B. Williams, has amassed quantities of data from which it may be deduced that on the average one cannot expect to achieve a value of PE_s lower than 0.62 second for pointing at a distant outdoor target with the air-column-present method [1 and 2]. As the air column contributes substantially to the value of PE_s, it is interesting to consider the possible effect of magnification on outdoor pointing accuracy. In the work on precision of outdoor pointing [1 and 2], the value $PE_s=\pm 0.62$ second, was reported as the value determined for a telescope with magnification of 37 diameters from 4,750 pointings. In the study of the effect of magnification on pointing accuracy for

indoor targets [3], the value of PE_s was found to vary inversely with the magnification. For magnification 37, the contribution of the telescope alone is 0.14 second, neglecting the constant term. The contribution of the air column alone is then

$$PE_s(\text{air column}) = \sqrt{(0.62)^2 - (0.14)^2} = 0.60 \text{ second.} \quad (3)$$

Clearly then the air column was contributing the major portion of the error in this instance.

If it is assumed that the contribution from the air column was constant on the average, then the approximate effect of magnification on PE_s for outdoor targets may be predicted from the equation

$$PE_s = \sqrt{\left(\frac{4.96}{M}\right)^2 + (0.60)^2}. \quad (4)$$

The values of PE_s predicted by eq 4 for a series of magnifications varying from 5 to 100 are listed in table 3. To present a more complete picture, the table lists values for four different values of the air-column contribution. Column 2 gives the values for zero air-column contribution, which is closely approximated in indoor pointing. Column 3 shows the expected values of PE_s versus magnification for an air column effect of 0.48 second. This is a close approximation to the air column contribution that may be expected for ranges of 100 to 1,000 meters under average weather conditions. Column 4 shows the expected values of PE_s for an air column effect of 0.60 second. This is the average air column contribution that may be expected as an average for all ranges under average weather conditions, or more specifically for the range 1,000 to 4,500 meters. Column 5 shows the expected values of PE_s for an air column effect of 0.71 second. This is the average air column contribution that may be expected for ranges in excess of 4,500 meters under average weather conditions.

These results are shown graphically in figure 3. Consideration of curves 2, 3, and 4 shows clearly that the gain in precision for outdoor pointings for magnifications above 30 diameters is negligible. Even for a magnification as low as 12 diameters, the values of PE_s for the three cases illustrated are 31, 22, and 15 percent higher than would be expected for a magnification of 100 diameters. It is of interest to determine the values of the magnification for which the error for the telescope alone is equal to the error resulting from the air column alone for these three cases. This was done by noting the value of the magnification for which the value of PE_s is 1.4 times the value of PE_s for the air column alone. For curves 2, 3, and 4, this condition was satisfied by magnifications of 11, 8.5, and 7.5 diameters, respectively. For magnifications greater than these, the error resulting from the influence of the air column predominates, and relatively small gain in precision of pointing results with increasing magnifi-

TABLE 3.—*Predicted values of the probable error, PE_s, for an outdoor target as a function of magnification*

	Probable error of a single pointing			
	Telescope alone	Telescope and air column		
PE_s (air column) sec[1]	0.00	0.48	0.60	0.71
	Sec	*Sec*	*Sec*	*Sec*
100	0.05	0.48	0.60	0.71
48	.10	.49	.61	.72
37	.13	.50	.62	.72
30	.16	.51	.63	.73
24	.21	.52	.64	.74
20	.25	.54	.65	.75
15	.33	.58	.68	.78
12	.41	.63	.73	.82
10	.50	.69	.78	.86
5	.99	1.10	1.16	1.22

[1] Magnification diameters given in first column.

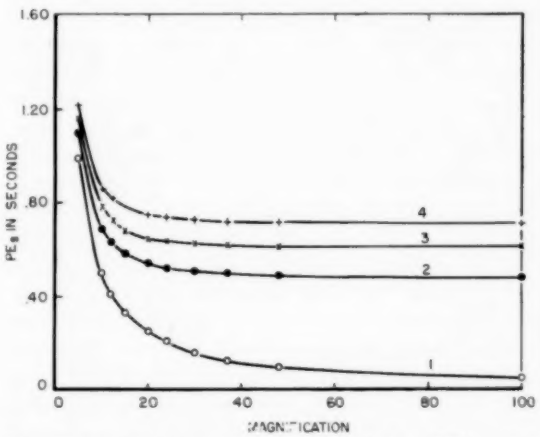

FIGURE 3.—*Probable error of a single pointing (PE_s) versus magnification.*

Curve 1 shows the variations of PE_s with magnification for air column eliminated. Curves 2, 3, and 4 show the variation of PE_s with magnification for errors arising from influence of the air column of 0.48, 0.60, and 0.71 second, respectively.

cation. For lower values of the magnification the effect of the telescope alone predominates, and appreciable gains in the precision of pointing may be obtained by increasing the magnification until these values are reached.

IV. Conclusions

The turbulence of the column of air intervening between observer and target is the principal factor that places a limit on the ultimate accuracy in the outdoor pointing of a telescope. The effect of the intervening air column is so great that the lowering of values of PE_s that might be expected with increasing magnification is, for all practical purposes, completely masked for all magnifications above 30 diameters. In fact, judging by the values liste in table 3, it is probable that a magnification of diameters is adequate at least 90 percent of t time in that the average value of PE_s for outdo pointing in the daytime is only 0.04 second high for magnification 20 than can be expected for magnification of 100 diameters.

V. References

[1] E. E. Washer and H. B. Williams, J. Opt. Soc. Am. 3 400 (1946).

[2] F. E. Washer and H. B. Williams, J. Research NBS 3 479 (1946) RP1717.

[3] F. E. Washer, J. Research NBS **39**, 163 (1947) RP 182

Washington, June 24, 1947.

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Research Paper RP1830
Volume 39, October 1947

Part of the Journal of Research of the National Bureau of Standards

Alkylbenzenes in the C_8 Fraction From Five Different Catalytic Petroleum Refining Processes[1 2 3]

By Anton J. Streiff [4] and Frederick D. Rossini

This report gives the results of the analysis, by measurements of freezing points of appropriate mixtures, supplemented by analytical distillation, of the four individual C_8 alkylbenzenes (ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene) occurring in the product from the following five different catalytic petroleum refining processes: (1) Hydroforming, (2) Two-pass Fixed Bed, (3) Three-pass Fixed Bed, (4) Low-temperature Fluid, and (5) High-temperature Fluid. The data indicate that the relative amounts by volume of the four C_8 alkylbenzenes are not greatly different in the five different products being, on the average, as follows: ethylbenzene, 12; *o*-xylene, 21; *m*-xylene, 48; *p*-xylene, 19. These amounts correspond substantially to those called for in chemical thermodynamic equilibrium for the operating temperatures involved.

I. Introduction

As part of its war research program, the American Petroleum Institute Research Project 6 at the National Bureau of Standards was requested to analyze the individual alkylbenzenes in the C_8 fraction from five different catalytic petroleum refining processes. The investigation was completed early in 1943, and the results on the composition were correlated, by appropriate other laboratories, with manufacturing conditions and with engine performance, to improve the utility of these materials as components for aviation fuel. This report gives the results of the analysis of the amounts of ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene in the product from these five different catalytic petroleum refining processes.

II. Materials Analyzed

The five lots of material that were analyzed in this investigation are listed in table 1, which gives the name of the process that produced the material, the name of the company that supplied the sample, the approximate temperature and pressure in the reaction zone, and the charging stock.

The process labeled hydroforming is one in which material of the gasoline range is reformed, in the presence of a catalyst and hydrogen, to give material of nearly the same boiling range but of appreciably higher aromatic content.

The process labeled two-pass fixed bed is a catalytic-cracking one of Houdry design, in which material of the gas oil or heavier distillate range is cracked in the presence of a catalyst in a fixed bed, with the gasoline fraction from the first operation repassed through a similar operation.

The process labeled Three-pass Fixed Bed is also a catalytic cracking process of Houdry design and is operated similarly. The charging stock for this process was heavy naphtha accumulated from the two-pass fixed bed process.

The process labeled Low-temperature Fluid and the one labeled High-temperature Fluid are catalytic cracking processes in which a fluid catalyst is moved continuously through the reaction zone, with the catalyst being reactivated in continuous flow through a separate chamber. The charging stock here is kerosine or gas oil.

All of the foregoing processes have been described many times in technical articles in the petroleum journals, and readers will readily find them under the names given above or the follow-

[1] This investigation was performed as part of the work of the American Petroleum Institute Research Project 6 at the National Bureau of Standards on the Analysis, Purification, and Properties of Hydrocarbons.

[2] This paper is a revision of a restricted report of the American Petroleum Institute Research Project 6 at the National Bureau of Standards issued under date of July 31, 1943, with the title "Analysis of the Aromatic Hydrocarbons in the C_8 Fractions of High Aromatic Stocks from Five Different Plant Processes."

[3] Presented before the Division of Petroleum Chemistry of the American Chemical Society at the meeting at Atlantic City, N. J., in April 1947.

[4] Research Associate on the American Petroleum Institute Research Project 6.

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TABLE 1. *Information concerning the samples analyzed*

Catalytic petroleum refining process	Supplier	Temperature in reaction zone (approximate)			Pressure in reaction zone		Charging stock
		°F	°C	°K	lb/in.² (gage)	atm	
Hydroforming	Humble Oil and Refining Co., Houston, Tex.	925	496	769	215	15.6	Selected naphtha.
Two-pass fixed bed	Sun Oil Co., Marcus Hook, Pa	850	454	727	50	4.4	Gas oil plus heavy distillate from Mi continent and Gulf coast crudes.
Three-pass fixed bed	Socony-Vacuum Oil Co., Paulsboro, N. J.	875	468	741	33	3.2	Heavy naphtha from two-pass fix bed catalytic process.
Low-temperature fluid	Standard Oil Development Co., Elizabeth, N. J.	800	427	700			Mirando kerosine.
High-temperature fluid	Standard Oil Development Co., Elizabeth, N.J.	975	524	797			Southwest Louisiana gas oil.

ing: Hydroforming petroleum refining process; Houdry catalytic cracking process; fluid catalytic cracking process.

Each of the five materials analyzed may be described as that part of the product of the given plant process containing all of the four C_8 aromatic hydrocarbons, which have normal boiling points as follows: Ethylbenzene, 136.19° C; *o*-xylene, 144.42° C; *m*-xylene, 139.10° C; *p*-xylene, 138.35° C. Each sample was prepared by the supplier by distillation of the whole product from the given plant process. A small amount of toluene (at 110.62° C) and a small amount of isopropylbenzene (at 152.40° C) and higher C_9 alkylbenzenes were included in the material blended to form the sample for analysis in the present investigation, in order to insure the presence in the given sample of substantially all of the C_8 aromatic hydrocarbons from the original stock. Because some of the samples were prepared so as to include more C_7 and C_9 aromatics than others, the relative amounts of the C_7 and C_9 aromatics to the C_8 aromatics have no significance. Likewise, the aromatic content of the original material as submitted for analysis would depend upon how much of the C_7 and C_9 hydrocarbons (aromatics plus paraffins and naphthenes) was included.

The data that have an important significance are the relative amounts of the four C_8 alkylbenzenes in the five samples.

III. Method of Analysis

The method of analysis developed for this investigation is as follows:

(a) A sample of the material is subjected to an analytical determination of the aromatic content by adsorption [1][5]. The amount of materi processed in the adsorption experiment is selecte so as to produce not less than 15 ml of a portio that contains all the aromatics, with only a smal amount or none of the nonaromatic hydro carbons. The results of the analytical adsorptio experiment on the sample from the Hydroforming process are shown in figure 1, and the correspon ing results on the sample from the High-tempera ture Fluid process are shown [6] in figure 2.

(b) Using the aromatic portion obtained a described in (a), experiments are made to deter mine the lowering of the freezing point of sample of "pure" ethylbenzene, *p*-xylene, *m*-xylene, an *o*-xylene, respectively, produced by the addition small measured amounts (in the range 5 to 7 per cent) of the given unknowns to the given "pure compounds. Each such measurement of th lowering of the freezing point produces a value o the amount of the given hydrocarbon in the un known mixture. This procedure requires that th molecular weight of the unknown be known. I it is not known, a determination of the molecula weight may be made by measuring the lowering o the freezing point produced by the addition of small measured amount of the given unknown t "pure" benzene (provided benzene is known no to be a component of the unknown). This metho of determining individual hydrocarbons in mix tures of hydrocarbons by measurement of freezing points is described in detail in reference [2]. The "unknown" sample for which complete data are

[5] Figures in brackets indicate the literature references at the end of thi paper.

[6] If, as may be probable, there is no significant difference between the rela tive amounts of the four C_8 aromatic hydrocarbons at the front and back end of the aromatic plateau from the adsorption experiment, then the aromati portion may be taken substantially free of nonaromatic compounds.

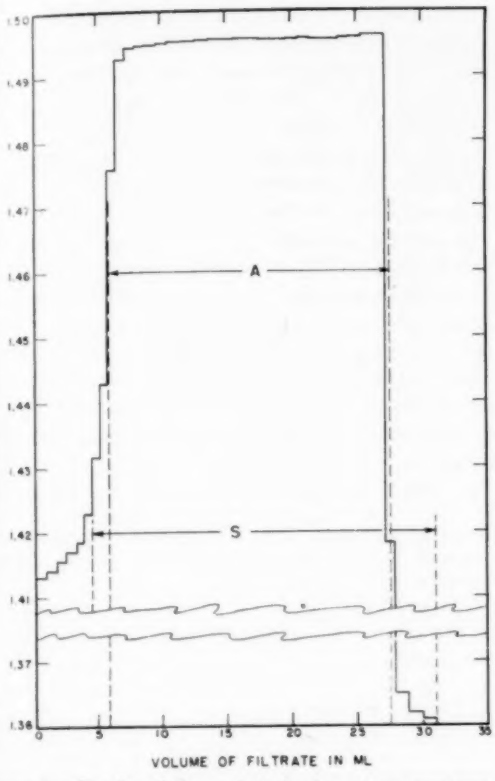

FIGURE 1.—*Results of the analytical adsorption experiment on the sample from the Hydroforming process.*

The refractive index of the filtrate is given as a function of its volume. The volume represented by A measures the aromatic content of the material. The volume constituted by S shows the material that is to be mixed to constitute the sample of aromatic hydrocarbons (after the ethyl alcohol at the tail end is removed by washing).

given in table 1 of [2] is the Two-pass Fixed-Bed sample listed in table 1 of this report.

Although the foregoing represents the procedure finally selected as being the best for analyses of the kind described, actually many more observations of other kinds were made on the materials in order to work out the simplest and most reliable method of analysis. For example, in order to obtain larger quantities of the aromatic portion than are recommended above, the separation of the nonaromatic hydrocarbons from the aromatic hydrocarbons was also performed by a method previously described [3]. This method involves separation of the nonaromatic hydrocarbons from the aromatic hydrocarbons in the adsorption column by displacement with pentane, the subsequent removal of the hydrocarbons from the adsorption column with methanol and the removal from the aromatic hydrocarbons of methanol by extraction with water and of pentane by distillation. The use of this procedure is also described in reference [5].

The aromatic content was determined not only by the simple adsorption procedure described under (a) above, but also by comparison of the refractive index of the original material with the refractive index of mixtures made by remixing known amounts of the aromatic portion and the nonaromatic portion, obtained as described in the preceding paragraph.

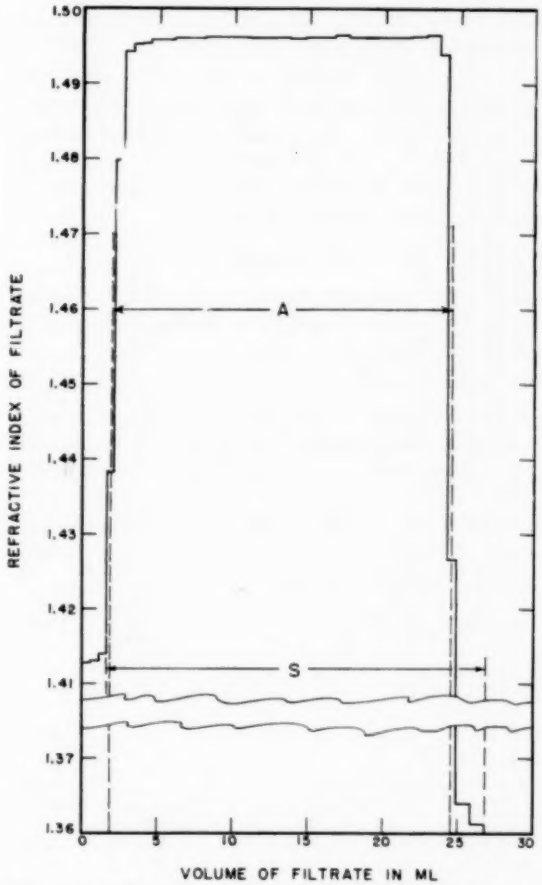

FIGURE 2.—*Results of the analytical adsorption experiment on the sample from the High-temperature Fluid catalytic cracking process.*

The refractive index of the filtrate is given as a function of its volume. The volume represented by A measures the aromatic content of the material. The volume constituted by S shows the material that is to be mixed to constitute the sample of aromatic hydrocarbons (after the ethyl alcohol at the tail end is removed by washing).

The amounts of toluene, of the sum of ethylbenzene plus *p*-xylene plus *m*-xylene, of *o*-xylene, and of the C_9 aromatics in the aromatic portion, were determined by an analytical distillation of about 180 ml of the aromatic portion at a high reflux ratio in a rectifying column of high efficiency and low hold-up, using *n*-decane or diethyl-benzene as a "chaser". These distillations were performed, under the supervision of C. B. Willingham, in distilling columns identical with still No. 2 described in table 1 of reference [4]. The results of these distillations (except for the relative amounts of the components) were similar to the results presented in figures 8 to 14, inclusive, of reference [6].

The molecular weights of the given aromatic portions were calculated from the relative amounts of the C_7, C_8, and C_9 aromatic hydrocarbons as determined from the distillation and also from measurements of the lowering of freezing point in benzene, as described in (b) above.

IV. Results

The values of the bromine number, and the content of olefins, aromatics, and paraffins plus naphthenes, for the materials as received, are given in table 2.

TABLE 2.—*Content of olefin, aromatic, and paraffin plus naphthene hydrocarbons in the samples as received*

Sample	Bromine number [a]	Content of olefins [b]	Content of aromatics [c]	Content of paraffins plus naphthenes (by difference)
	g/100 g	*Percentage by vol.*	*Percentage by vol.*	*Percentage by vol.*
Hydroforming	0.30	0.4±0.1	(I) 91.8±0.5 (II) 91.3± .5 Mean 91.6± .4	8.0±0.4
Two-pass fixed bed	1.59	1.4± .2	(I) 55.2± .5 (II) 55.5± .5 Mean 55.3± .4	43.3± .4
Three-pass fixed bed	1.15	1.0± .2	(I) 85.3± .5 (II) 86.3± .5 Mean 85.8± .4	13.2± .4
Low-temperature fluid	3.84	3.5± .3	(I) 77.2±1.0 (II) 79.0±1.0 Mean 78.1± .7	18.4± .8
High-temperature fluid	15.06	13.5±1.0	(I) 78.4±1.0 (II) 80.4±1.0 Mean 79.4± .7	7.1±1.2

[a] Determined by R. C. Hardy, Section 3.5, National Bureau of Standards.
[b] Calculated assuming the olefins to be C_8H_{16} and the ratio of the density of the aromatics to the olefins to be 1.18.
[c] Determined independently in two ways, (I) giving values obtained by the simple adsorption experiments (performed by B. J. Mair) described in this report, and (II) giving values obtained by refractive index measurements on the original material and appropriate mixtures of the aromatic and nonaromatic portions of the original material.

The amounts of C_7, C_8, and C_9 aromatic hydrocarbons in the aromatic portion of each material as determined from the analytical distillations, are given in table 3. This table also gives values for the molecular weight of the aromatic portion as calculated from the data from the analytical distillation and as determined from measurements of the lowering of the freezing point in benzene.

In table 4 are given values of the amounts of each C_8 aromatic hydrocarbon determined to be in the aromatic portion by means of measurements of freezing points, and the sum of the amounts of the four C_8 aromatic hydrocarbons as so determined. It is interesting to note the good accord between the values given in the last column of table 4 with the corresponding values given in the third column of table 3.

In table 5 is given a comparison of the content of

TABLE 3.—*Amounts of the C_7, C_8, and C_9 aromatic hydrocarbons in the aromatic portion, and the molecular weight of the aromatic portion*

Sample	Amounts (% by volume) of aromatic hydrocarbons—			Molecular weight of the aromatic portion [a]	
	C_7	C_8	C_9	I	II
				g/mole	*g/mole*
Hydroforming	0.7±0.3	94.4±0.5	4.9±0.5	106.65	107.36
Two-pass fixed bed	3.3± .5	85.0± .5	11.7± .5	107.06	107.31
Three-pass fixed bed	2.9± .5	94.2± .5	2.9± .5	106.05	105.98
Low-temperature fluid	0.5± .3	97.3± .5	2.2± .5	106.34	105.96
High-temperature fluid	0.5± .3	97.9± .5	1.6± .5	106.27	106.04

[a] Determined independently in two ways, column I giving values calculated from the distillation data, and column II giving values determined from the lowering of the freezing point in benzene, as described in part III of reference [3]. The molecular weight of a C_8 aromatic is 106.16.

TABLE 4.—*Amounts of the four C_8 alkylbenzenes in the aromatic portion, as determined from freezing-point measurements*

Sample	Ethylbenzene	*p*-Xylene	*m*-Xylene	*o*-Xylene	Total of C_8 aromatics
	Percentage by volume [a]				
Hydroforming	11.2±1.2	17.2±1.2	45.1±1.2	23.5±1.2	97.0±2.4
Two-pass fixed bed	11.4±1.2	16.4±1.2	41.4±1.2	16.9±1.2	86.1±2.4
Three-pass fixed bed	8.0±1.2	18.9±1.2	48.5±1.2	17.6±1.2	93.0±2.4
Low-temperature fluid	12.9±1.2	17.5±1.2	45.7±1.2	24.3±1.2	100.4±2.4
High-temperature fluid	12.4±1.2	19.4±1.2	48.6±1.2	17.7±1.2	98.1±2.4

[a] The uncertainty of ±1.2 percent assigned to the amount of each C_8 aromatic hydrocarbon in the aromatic portion is the resultant of an estimated uncertainty of ±1.0 percent in the determination of the lowering of the freezing point and of ±0.5 percent in the determination of the molecular weight of the unknown mixture.

o-xylene in the five materials as determined by measurements of freezing points and as determined from the data of the analytical distillation.

TABLE 5.—*Comparison of the content of o-xylene in the aromatic portion as determined (I) from the measurements of freezing points and (II) from the analytical distillation*

Sample	Amount of o-xylene	
	I	II
	Percentage by vol.	Percentage by vol.
Hydroforming	23.5±1.2	22.6±1.0
Two-pass fixed bed	16.9±1.2	17.6±1.0
Three-pass fixed bed	17.6±1.2	18.0±1.0
Low-temperature fluid	24.3±1.2	23.8±1.0
High-temperature fluid	17.7±1.2	17.6±1.0

TABLE 6.—*Relative amounts of the four C_8 alkylbenzenes as determined from freezing-point measurements* [a]

Sample	Ethylbenzene	p-Xylene	m-Xylene	o-Xylene	Total
	Percentage by volume				
Hydroforming	11.6±1.0	17.7±1.0	46.5±1.0	24.2±1.0	100
Two-pass fixed bed	13.2±1.0	19.1±1.0	48.1±1.0	19.6±1.0	100
Three-pass fixed bed	8.6±1.0	20.3±1.0	52.2±1.0	18.9±1.0	100
Low-temperature fluid	12.9±1.0	17.4±1.0	45.5±1.0	24.2±1.0	100
High-temperature fluid	12.6±1.0	19.8±1.0	49.6±1.0	18.0±1.0	100
Mean value	11.8	18.8	48.4	21.0	.....
Average difference between the mean and the individual values	±1.3	±1.0	±2.0	±2.6	.....
Maximum difference between the mean and the individual values	−3.2	+1.5	+3.8	+3.2	.....

[a] The values given in this table are those from table 4 recalculated to make the sum of the amounts of the four C_8 aromatics equal to 100 percent. The assigned uncertainty arises only from the determination of the lowering of the freezing point, since an uncertainty in the molecular weight of the unknown mixture of aromatic hydrocarbons does not affect the relative amounts of the four C_8 aromatic hydrocarbons.

In table 6 are given values for the relative amounts of the C_8 aromatic hydrocarbons in each of the five different materials, as determined from measurements of the lowering of the freezing point. At the bottom of table 6 are also given for each compound, for the five samples, (a) the mean value, (b) the average difference between the mean and the individual values, and (c) the maximum difference between the mean and the individual values.

V. Discussion

In connection with the results obtained in this investigation, the following conclusions may be drawn:

(a) The relative amounts of the four C_8 alkylbenzenes are nearly the same in the product from all five of the catalytic petroleum refining processes. This is clearly shown by the results in table 6, which gives the following for the mean value and for the average difference between the mean and the individual values: Ethylbenzene, 11.8, ±1.3; *p*-xylene, 18.8, ±1.0; *m*-xylene, 48.4, ±2.0; *o*-xylene, 21.0, ±2.6.

(b) The relative amounts of the four alkylbenzenes are, on the average, within the estimated limits of uncertainty, equal to the relative amounts that would be expected at thermodynamic equilibrium at the temperature at which the material was produced. This is clearly shown by the results given in table 7, which gives for each process the temperature, the actual amount, and calculated equilibrium amount for each of the four C_8 alkylbenzenes. The calculated values for thermodynamic equilibrium given in table 7 are taken from reference [7].

TABLE 7.—*Comparison of the actual composition with that calculated for thermodynamic equilibrium at the given temperature (Actual values from table 6 of this report; calculated values from reference [7])*

Sample	Temperature	Relative Amounts of the Four C_8 Alkylbenzenes							
		Ethylbenzene		p-Xylene		m-Xylene		o-Xylene	
		Actual	Calculated	Actual	Calculated	Actual	Calculated	Actual	Calculated
	°K								
Hydroforming	769	11.6±1.0	10.0±1.5	17.7±1.0	20.9±3.5	46.5±1.0	46.4±5.0	24.2±1.0	22.7±3.5
Two-pass fixed bed	727	13.2±1.0	9.0±1.5	19.1±1.0	21.2±3.5	48.1±1.0	47.3±5.0	19.6±1.0	22.5±3.5
Three-pass fixed bed	741	8.6±1.0	9.4±1.5	20.3±1.0	21.1±3.5	52.2±1.0	46.9±5.0	18.9±1.0	22.6±3.5
Low-temperature fluid	700	12.9±1.0	8.3±1.5	17.4±1.0	21.5±3.5	45.5±1.0	47.8±5.0	24.2±1.0	22.4±3.5
High-temperature fluid	797	12.6±1.0	10.7±1.5	19.8±1.0	20.6±3.5	49.6±1.0	45.9±5.0	18.0±1.0	22.8±3.5

VI. References

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Heat Capacities at High Temperatures of Uranium, Uranium Trichloride, and Uranium Tetrachloride

By Defoe C. Ginnings and Robert J. Corruccini

The enthalpies referred to 0° C of uranium in the range 0° to 900° C, of uranium trichloride in the range 0° to 725° C, and of uranium tetrachloride in the range 0° to 425° C, have been determined using the "drop" method with an ice calorimeter. Derived values of entropy referred to 0° C and specific heat are given. The samples were of high purity. Two first-order transformations of uranium were observed and the heats of transition calculated from the experimental data. No evidence of first- or second-order transitions in the chlorides was found.

I. Introduction

This research was undertaken as a part of a program sponsored by the Manhattan District, U. S. Army Corps of Engineers. A portion of the information given in this paper will appear in Division VIII of the Manhattan Project Technical Series. The following report has been declassified by the Atomic Energy Commission.

II. Method and Apparatus

The method and apparatus have been described previously.[1] [2] In brief, the method consisted in heating the sample in a furnace to a known temperature and dropping it into an ice calorimeter that measured the heat evolved in cooling the sample to 0° C. The calorimeter was calibrated electrically. The sample was sealed in a Nichrome–5 capsule having a screw cap and gold gasket. The heat capacity of the empty capsule and the heat lost by the container during the drop were accounted for by "blank" experiments made with the empty capsule. The temperature of the sample in the furnace was measured by a platinum platinum-rhodium thermocouple that had been calibrated at the National Bureau of Standards.

[1] D. C. Ginnings and R. J. Corruccini, J. Research N. B. S. **38**, 583 (1947) RP1796.
[2] D. C. Ginnings and R. J. Corruccini, J. Research N. B. S. **38**, 593 (1947) RP1797.

III. Materials

1. Uranium

The uranium sample, furnished by H. E. Cleaves of the National Bureau of Standards, was in the form of rods having a diameter of ⅛ in. A spectroscopic analysis of a clean sample of uranium taken from the same batch showed impurities of 0.03 percent to 0.04 percent, including carbon, 0.015 percent; hydrogen, 0.0005 percent; nitrogen, 0.003 percent; and oxygen, 0.002 percent. These impurities were the most significant in computing the correction for impurity to be applied to the enthalpy.

2. Uranium Trichloride

The uranium trichloride sample was obtained from E. C. Evers of Brown University and was of the highest obtainable purity. It was prepared from sublimed uranium tetrachloride by reduction with hydrogen and was received in the form of a crystalline powder in a sealed glass bottle, which was kept in a desiccator. The following chemical analysis was received with the sample: U+Cl=99.97 percent; atom ratio Cl/U=3.001; material insoluble in water=0.13 percent, calculated as UO_2. A portion of the sample was transferred to the Nichrome capsule in a drybox containing P_2O_5, helium was admitted and the

capsule was sealed. At the time of the transfer, another portion of the sample was taken for further analysis. The analysis (performed under the direction of J. J. Tregoning of the National Bureau of Standards) gave U+Cl=99.50 percent, atom ratio Cl/U=2.999, material insoluble in water=0.55 percent, calculated as UO_2. A spectrographic analysis performed at the same time indicated a total of about 0.08 percent miscellaneous metal impurities (mainly Ca, 0.01 %; Fe, 0.013 %; Mg, 0.01 %; Na, 0.02 %; and Si, 0.006 %) and confirmed the belief that the principal metallic constituent of the water-insoluble material was uranium.

3. Uranium Tetrachloride

The uranium tetrachloride was distilled in Pyrex in vacuum from a sample bearing the analysis, U+Cl=99.50 percent, atom ratio U/Cl=3.997. A small amount of reddish solid that was more volatile than the uranium tetrachloride was discarded in this process, as well as nonvolatile products such as UO_2. (The UO_2 would result from contamination of the sample with water, followed by hydrolysis.) Uranium tetrachloride is extremely hygroscopic. At the close of the distillation, the receiver was sealed. It was next opened in a drybox containing P_2O_5, the sample pulverized with a steel rod, and a portion transferred to the Nichrome capsule, helium was admitted and the capsule was immediately sealed. Samples taken before and after the filling of the capsule gave essentially identical chemical analyses averaging U+Cl=99.97 percent, atom ratio Cl/U=4.003. A spectrographic analysis made at the same time indicated the presence of 0.1 percent of miscellaneous metals (mainly Fe, 0.05 percent; Na, 0.02 percent; Ca, 0.01 percent; Mg, 0.01 percent; Al, 0.005 percent) and 0.1 to 1 percent of Ni. At the completion of the experimental work, the sample was removed from the capsule in the drybox and again analyzed, giving U+Cl=99.64 percent, atom ratio Cl/U=4.023.

IV. Results

Table 1 gives the results of the individual experiments. The "apparent" calibration factor [3] of the ice calorimeter was taken as 64.638 calories per gram of mercury (1 cal=4.1833 int joule). In columns 2 and 3 are given the masses of mercury after small corrections have been applied for buoyancy, heat leak, change in level of mercury meniscus, variation in capsule weight, and variation in the amounts of gas and gold contained in the capsule. As these corrections are in most cases so small as to be barely significant, they are not listed separately. They are approximately the same as in a previous report.[4] The masses at a given temperature are listed in the order in which the experiments were performed, although this is not true of the order in the table as a whole.

1. Uranium

The first series of experiments extended up to 756.7° C, and was made with a sample of uranium that had been pickled in nitric acid to remove the surface film of oxide. The air in the capsule was replaced with helium before sealing. It was found in experiments at 790° C that the uranium was attacking the Nichrome capsule. A second series of experiments in the range 723.9° to 898.6° C was then made with a portion of the sample on which a thin protective film of oxide had been formed. In addition, the bottom of the capsule was covered with a layer of BeO (about 1 g) in order to reduce the contact between the uranium and the capsule. There was no evidence of attack with these precautions. The BeO was kept in the capsule during the blank experiments of the second series.

TABLE 1.—*Results of individual experiments*

Temperature	Mass of Mercury			$(H-H_{0°C})$		
	Blank experiments	Experiments with sample	Net	Observed [a]	Calculated [b]	Observed minus calculated
URANIUM, SERIES A (58.7768-GRAM SAMPLE)[c]						
°C	g	g	g	cal g⁻¹	cal g⁻¹	Percent
110.6	1.4825 [e] 1.4909 1.4798 1.4823 1.4820	[d] 4.3441 4.3425 4.3477 4.3470	2.8635	3.1421	3.1419	+0.0
200.8	2.7659 2.7671 2.7658 2.7646	[d] 8.1192 8.1258 8.1249 8.1242	5.3583	5.8797	5.8812	−.0
300.9	4.2401 4.2392 4.2404	[d] 12.5696 12.5730 12.5763 [f] 12.5743 [f] 12.5723	8.3336	9.1445	9.1437	+.0

See footnotes at end of table.

[3] See footnote 1.

[4] See footnote 2.

TABLE 1.—*Results of individual experiments*—Continued

Temperature	Mass of Mercury: Blank experiments	Mass of Mercury: Experiments with sample	Mass of Mercury: Net	$(H-H_{0°C})$: Observed [a]	$(H-H_{0°C})$: Calculated [b]	Observed minus calculated
URANIUM, SERIES *A* (58.7768-GRAM SAMPLE) [c]—Continued						
426.8	6.1709 6.1731 6.1787	18.6040 18.6098 [d] 18.6128 [f] 18.5903	12.4317	13.6413	13.6392	+.02
579.2	8.6187 8.6193 [d] 8.6243	[d] 26.6812 26.6837 26.6782	18.0612	19.8186	19.8196	−.01
637.9	[g] (9.619)	[f] 30.1245	20.506	22.501	22.501	.00
657.2	[g] (9.956)	31.3063	21.350	23.427	23.428	.00
676.5	[g] (10.293)	35.0466	24.754	27.163	27.160	+.01
700.2	[g] (10.714)	36.3865	25.673	28.171	28.170	.00
723.9	11.1386 11.1420 11.1336	37.7187 37.7279	26.5852	29.1719	29.1801	−.03
756.7	[h] (11.727)	39.5975	27.871	30.583	30.578	+.02
URANIUM, SERIES *B* (40.4032-GRAM SAMPLE) [c]						
723.9	15.6009 15.6041	[d] 33.9078 33.8997	18.2999	29.172	29.180	−0.03
789.2	17.2651	40.2712	23.0061	36.674	36.652	+.06
807.7	17.7361	41.1632	23.4271	37.345	37.363	−.05
853.4	[18.9062 18.9184	43.4475	24.5321	39.106	39.119	−.03
898.6	20.0762	45.7132	25.6370	40.866	40.856	+.02
URANIUM TRICHLORIDE (16.4069-GRAM SAMPLE) [c]						
50.3	0.6995 .7003 .7002 .6996	1.6051 1.6061 1.6066	0.9060	3.5633	3.5644	−0.03
110.5	1.5633 1.5614 1.5626	3.5626 3.5625 3.5619	1.9999	7.8636	7.8649	−.02
209.7	2.9156 2.9154 2.9175	6.5816 6.5786 6.5777	3.6631	14.4012	14.3870	+.10
309.9	4.4770 4.4751 4.4792	10.0081 10.0114 10.0097	5.5326	21.7466	21.7539	−.03
426.7	6.5116 6.5181 6.5142 [d] 6.5168 6.5160 6.5156 6.5205	14.4529 14.4511 14.4517 [i] 14.4329 [i] 14.4314 [i] 14.4329	[j] 7.9358	31.1895	31.2041	−.05
498.9	[g] (7.719)	[i] 17.0490	[j] 9.353	36.761	36.747	+.04
597.0	9.0976 9.0968 9.0885 9.0923 9.0918	20.0554 20.0555 20.0497	10.9601	43.076	43.035	+.09
676.4	10.8650 10.8546 10.8563	23.8144 23.8248 23.8148	12.9594	50.933	50.991	−.11
723.8	11.7580 11.7650	25.7606 25.7451 25.7422	[i] 14.0155	55.084	55.053	+.06

See footnotes at end of table.

TABLE 1.—*Results of individual experiments*—Continued

Temperature	Mass of Mercury: Blank experiments	Mass of Mercury: Experiments with sample	Mass of Mercury: Net	$(H-H_{0°C})$: Observed [a]	$(H-H_{0°C})$: Calculated [b]	Observed minus calculated
URANIUM TETRACHLORIDE (16.8451 GRAM SAMPLE) [c]						
50.3	0.7059 .7051 .7080	1.7081 1.7102 1.7106	1.0033	3.8333	3.8333	0.00
110.5	1.5792 1.5763 1.5780	[e] 3.8083 [d] 3.8197 [d] 3.8223 3.8179 3.8191	2.2415	8.5641	8.5635	+.01
200.7	2.9393 2.9445 2.9457 2.9487 2.9431 2.9445 2.9416	7.0878 7.0909 7.0922 7.0908	4.1465	15.8425	15.8443	−.01
211.3	[g] (3.107)	7.4860 7.4876	4.380	16.733	16.714	+.11
221.8	[g] (3.270)	7.8796 7.8839	4.612	17.620	17.578	+.23
300.9	4.5173 [d] 4.5180 4.5188	[d] 10.8522 10.8463 10.8533	6.3324	24.194	24.193	.00
374.2	5.7009 5.7092 [d] 5.7036	13.6842 [d] 13.6808 13.6826	7.9781	30.482	30.483	.00
426.7	6.5659 6.5670 6.5690	[d] 15.7525 15.7510 15.7480	9.1826	35.084	35.083	.00

[a] Corrected for impurity.

[b] In the cases of α-uranium and UCl_3, these data were obtained by interpolation in the smoothed tables of enthalpy before rounding off and with allowance for curvature. In the cases of β and γ-uranium and UCl_4, these values were calculated from equations that were fitted to the observed data See text.

[c] Corrected for buoyancy.

[d] Weighted less due to unsteady heat leak.

[e] Discarded according to Chauvenet criterion.

[f] These experiments followed experiments at temperatures above the first transition.

[g] Interpolated.

[h] Extrapolated.

[i] These experiments followed those at 723.8° C, and are considered to be affected by corrosion of the capsule by the UCl_3 at that temperature.

[j] Corrected for effect of corrosion of the capsule. See text.

The second series gave a result at 723.9° C that was 0.14 percent higher than that obtained in the first series. This difference could have been caused by only one part in 10,000 (by weight) of oxygen, present as U_3O_8. Accordingly, the difference was attributed to the oxide film on the sample used in the second series and all results obtained in this series were corrected by −0.14 percent. In addition, an estimated correction of −0.21 percent for the impurities shown in the spectrographic analysis was applied to all results with uranium.

TABLE 2.—*Enthalpy, specific heat, and entropy at even temperature intervals (1 cal=4.1833 int j; 0°C=273.16°K)*—

t	$H-H_{0°C}$	C_p	$S-S_{0°C}$
URANIUM			
(°C)	cal g^{-1}	cal g^{-1} deg^{-1} C	cal g^{-1} deg^{-1} K
0	0	0.0275	0
50	1.393	.0283	.00469
100	2.831	.02919	.008819
150	4.317	.03022	.012552
200	5.856	.03135	.015988
250	7.453	.03257	.019197
300	9.113	.03388	.022228
350	10.841	.03529	.025119
400	12.642	.03681	.027900
450	14.521	.03846	.030595
500	16.486	.04031	.033226
550	18.552	.04253	.035819
600	20.750	.04521	.038403
650	23.080	.04818	.041001
668 (α)	23.965	.0193	.04194
[Transition	ΔH=2.83		ΔS=0.00301]
668 (β)	26.797	0.04262	0.04495
700	28.161	.04262	.04637
750	30.292	.04262	.04851
774 (β)	31.316	.04262	.04950
[Transition	ΔH=45.5		ΔS=0.00454]
774 (γ)	36.067	.03843	.05401
800	37.067	.03843	.05498
850	38.989	.03843	.05673
900	40.910	.03843	.05840
URANIUM TRICHLORIDE			
0	0	0.0706	0
50	3.543	.07112	.01191
100	7.112	.07167	.02218
150	10.709	.07224	.03123
200	14.336	.07284	.03933
250	17.995	.07348	.04667
300	21.687	.07416	.05340
350	25.414	.07489	.05963
400	29.178	.07568	.06544
450	32.982	.07655	.07089
500	36.832	.07755	.07604
550	40.738	.07877	.08094
600	44.716	.08036	.08564
650	48.790	.08256	.09018
700	52.994	.08573	.09460
725	55.173	.08774	.09680
URANIUM TETRACHLORIDE			
0	0	0.0748	0
50	3.810	.07745	.01280
100	7.730	.07923	.02408
150	11.726	.08056	.03412
200	15.787	.08189	.04319
250	19.916	.08329	.05149
300	24.116	.08473	.05916
350	28.389	.08617	.06630
400	32.734	.08762	.07301
425	34.933	.08834	.07622

The two transitions of uranium were clear-cut with no evidence of pretransition effects. No attempt was made to determine closely the temperatures of the transitions. For the purpose of calculating the heats of transition, the values 668° and 774° C were used for the transition temperatures. These were estimated from measurements by Dahl and Van Dusen[5] of the variation of electrical resistance of uranium with temperature and may be in error by a few degrees.

The results at temperatures below the first transition cannot be closely represented by a simple equation. Enthalpies at even temperature intervals were obtained by graphical interpolation and smoothed by adjustment of differences. The specific heat, C_p, and entropy referred to 0°C, $S-S_0°_C$, were derived graphically from the enthalpies in this temperature range. The results are given in table 2.

At temperatures above the first transition but below the second, the observed values of enthalpy in calories per gram, referred to the α-form at 0°C, are represented within 0.03 percent by the equation (fitted by the method of least squares)

$$H-H_{0°C}=-1.675+0.04262t(\beta\text{-form}),$$

where t is in deg C. Correspondingly,

$$C_p=0.04262(\beta\text{-form})$$

$$S-S_{0°C}=\int_{668}^{T}[C_{p(\beta)}/T]dT+[S_{(\beta)668°}-S_{(\alpha)0°C}](\beta\text{-form})$$

$$S-S_{0°C}=0.098144\log_{10}T-0.24690(\beta\text{-form}),$$

where T is in degrees Kelrin, taking 0°C as 273.16°K.

At temperatures above the second transition, the observed values of enthalpy referred to the α-form are represented within 0.06 percent by the equation (least squares)

$$H-H_{0°C}=6.326+0.03843t\ (\gamma\text{-form})$$

Correspondingly, $C_p=0.03843$ (γ-form)

$$S-S_{0°C}=\int_{774}^{T}[C_{p(\gamma)}/T]dT+[S_{(\gamma)774°}-S_{(\alpha)0°C}](\gamma\text{-form})$$

$$S-S_{0°C}=0.088481\log_{10}T-0.21318\ (\gamma\text{-form}).$$

Values calculated for even temperature intervals from the above equations are given in table 2.

The regularity of the data for the β and γ forms would seem to indicate that the two transformations were reversible under the experimental con-

[5] Andrew I. Dahl and Milton S. VanDusen, J. Research NBS **39**, 53 (1947) RP1813.

ditions. Certain experiments in the α range (noted in table 1) that were performed after the sample had been heated above the first transition show no significant abnormality.

It may be interesting to note that both the β and γ forms have not only constant values of C_p, but also have constant values of temperature coefficient of electrical resistance.[6] Also, the difference between the values of C_p for the two forms is 1.00 calories per degree-gram atom, which, within experimental error, is the value of $R/2$, where R is the universal gas constant. In the absence of complete information as to the crystal structures of the two forms, it is not possible to ascribe significance to the latter fact.

2. Uranium Trichloride

As it was expected that the capsule would be attacked to a slight extent by the UCl_3, the effect of this upon the enthalpy was tested by making a group of three experiments at 426.7° C at the beginning and a similar group at the end of the series of experiments with the sample. The average of the results of the final group was 0.14 percent lower than the average of the first group. No consistent variation was noted within either group alone, the maximum deviation from the mean of a group being 0.007 percent. On the other hand the results of the three experiments at 723.8° C showed a definite downward trend with the order performed over a range of 0.07 percent. It was assumed, therefore, that corrosion of the capsule at the higher temperatures had indeed affected the results. As there was no clear-cut evidence of a trend with time in the experiments at 579.0° and 676.4° C, it was assumed that all the corrosion had occurred during the experiments at 723.8° C. With some arbitrariness, the mass of mercury that would have been obtained in an experiment at 723.8° C in the absence of corrosion was taken to be 0.14 percent higher than the last result in the group at that temperature. The result at 498.9° C which was the only other one obtained following the experiments at 723.8° C was also corrected by +0.14 percent. At the close of the experiments, after removal of the sample from the capsule, it was found that the latter had lost 17.1 mg, or 0.2 percent, of its mass as a result of the corrosion.

[5] See footnote 5.

The correction for the impurities in the sample at the start of the experiments was somewhat uncertain because of the inconsistency of the two chemical analyses, the uncertainty as to the state of chemical combination of the spectrographically determined impurities, and the fact that the most probable forms (oxides or chlorides) of the latter have specific heats about three times that of UCl_3, which magnifies their effect upon the results. Fortunately, UO_2 has nearly the same specific heat (within 20 percent) as UCl_3, which reduces the uncertainty resulting from the variance in the amount of water-insoluble material found in the sample. Making reasonable assumptions with regard to the spectrographically determined impurities and employing the enthalpy data of Moore and Kelly[7] for UO_2, led to a total correction for impurities that ranged from −0.17 percent at 50.3° C to −0.24 percent at and above 426.7° C.

A smooth curve was drawn through a plot of $(H-H_{0°C})_{obs}/t$ versus t, values were read off at even temperature intervals and smoothed by adjustment of differences. The specific heat, $C_p=(\partial H/\partial T)_p$, was calculated from the smoothed values of enthalpy by the method of Rutledge[8] and $S-S_{0°C}=\int_0^t (C_p/T)dt$ was calculated by using Simpson's Rule.

The results are given in table 2.

3. Uranium Tetrachloride

The effect of possible reaction between the capsule and UCl_4 was tested by making a pair of experiments at 200.7° C early in the series of experiments with sample and a similar pair at the end of the series. The average of the second pair was only 2.1 mg, or 0.03 percent higher than the average of the first pair, which is as good agreement as could have been expected had the experiments been performed at the same time. Accordingly, no correction for corrosion of the capsule was applied. At the close of the series of experiments it was found that the capsule had lost 6.8 mg owing to corrosion, or only about one-third as much as for the UCl_3.

The correction for the impurities in the sample was subject to the same difficulties as for UCl_3. In addition, the chemical analyses were discordant in that they appeared to indicate a loss of 0.32 per-

[7] G. E. Moore and K. K. Kelley, J. Am. Chem. Soc. **69**, 2105 (1947).
[8] G. Rutledge, Phys. Rev. **40**, 262 (1932).

cent of uranium between the first and second analyses, the percentage of Cl remaining constant. Actually, there is every reason to believe that no detectable change in the sample occurred. The only reasonable alteration of the sample to expect would have been the loss of Cl (as HCl resulting from moisture absorption and hydrolysis) rather than the loss of uranium. Making reasonable assumptions with regard to the impurities led to a correction of −0.43 percent.

The mean specific heat, $(H-H_{0°C})_{obs}/t$, was found to be practically a linear function of temperature above 200° C. The following equation was fitted by trial and error (gram basis):

$$H-H_{0°C}=0.07605t+1.446\times10^{-5}t^2-0.00122t\times10^{-0.00516t-0.000027812}.$$

Correspondingly,

$$C_p=0.07605+2.891\times10^{-5}t-0.00122[1-2.3(0.00516t+0.0000556t^2)]\times10^{-0.00516t-0.000027812}.$$

Values were calculated from these equations at even temperature intervals and the entropy, $S-S_{0°C}$, obtained by Simpson's rule. The results are given in table 2.

V. Discussion

1. Accuracy

The instrumental error is about the same as in some previous measurements, where a more detailed discussion is given.[9] The error involved in measuring the temperature of the sample in the furnace contributes the major part of this uncertainty to which a value of about 0.2 percent may be assigned. In addition, the corrections for impurity have uncertainties of perhaps one-half their own magnitudes or 0.1 percent in the cases of uranium and UCl_3 and 0.2 percent for UCl_4. Taking all errors into account, the authors believe the corrected and smoothed enthalpies to be within 0.2 to 0.3 percent of the true values, except for the values at 50° C. At and below this temperature, the relative instrumental error is larger.

The specific heat and entropy possess a small additional uncertainty resulting from the fact that the derivative of a quantity can never be known as accurately as the quantity itself in the absence of a rigid mathematical formulation. This uncertainty becomes larger at the ends of the experimental ranges of the data, except for the high-temperature end of the uranium and UCl_4 data where linear representation of the enthalpy makes accurate differentiation possible. The heats of transition are accurate to perhaps 1 percent.

2. Comparison with other work

In none of the five known investigations presenting data comparable to those of this report was a correction applied for impurities, although only one of these authors [10] claimed to have a sample that was pure within analytical error. The heat capacities of uranium and its compounds are exceptionally sensitive to the presence of impurities, because the specific heats of the latter are usually several times as large as that of the pure uranium or uranium compound. As the samples used in the present investigation were of high purity, and as a correction was applied in each case to account for the presence of impurity, it was to be expected that the results of the other investigations, with the exception noted, would be the higher, calorimetric errors being left out of account.

In order to permit a condensed presentation of the data for comparison purposes, values of C_p and $(H-H_{0°C})/t$ in calories per degree-mole divided by the number of atoms per molecule are given in figure 1 for all three substances.

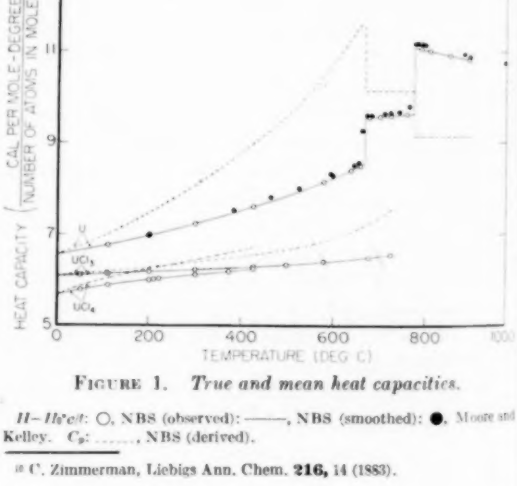

FIGURE 1. *True and mean heat capacities.*

H−H°/t: ○, NBS (observed): ——, NBS (smoothed): ●, Moore and Kelley. C_p: ……, NBS (derived).

[9] See footnote 2.

[10] C. Zimmerman, Liebigs Ann. Chem. **216,** 14 (1883).

(a) Uranium

The specific heat of a sample of unstated purity has been determined from low temperatures up to 27° C by E. A. Long, W. M. Jones, and J. Gordon [11] in the laboratory of W. F. Giauque at the University of California. Their values are lower than those of this investigation, the difference decreasing from 1.0 percent at 27° C to 0.3 percent at 0° C. These authors appear to claim an accuracy of 0.2 percent in this range. The specific-heat curve from the present investigation, if extrapolated downward, would become tangent to the above authors' results at about −30° C.

The enthalpy (referred to 25° C) of a 99.71-percent-pure sample has been measured at temperatures up to 1,000° C by Moore and Kelley.[12] These data were converted to the same basis as the enthalpy data of this paper by addition of the quantity, $H_{25°C}-H_{0°C}=0.688$ cal g^{-1}, taken from the report of Long, Jones, and Gordon.[13] The converted enthalpy data of Moore and Kelley were found to average 0.8 percent higher than those of the present investigation. The comparison is shown in figure 1, where the enthalpies have been converted to mean specific heats, $(H-H_{0°C})/t$, in order to give a representation that is more sensitive to the small differences between the two sets of data. For the β-form, the data of Moore and Kelley give $C_p=0.04360$ cal g^{-1} deg^{-1} C, that is, 2.3 percent higher than the value in this investigation. For the γ-form, Moore and Kelley's results give $C_p=0.03822$ cal g^{-1} deg^{-1} C, which is 0.5 percent lower than the value in this investigation. Comparison of the values of C_p for the α-form is not as informative, as Moore and Kelley's values must be obtained from an equation for the enthalpy that does not represent the data as closely as did the equations given by them for the higher forms.

The mean specific heat between 0° and 98.7° C was measured by Zimmerman,[14] who obtained 0.0277 cal g^{-1} deg^{-1} C as the mean of three experiments covering a spread of 1.5 percent. His sample reportedly was 100.0 percent pure. Blumcke [15] later disputed the interpretation of the data in these experiments and calculated the result to be 0.0280. These values are, respectively, 2 percent and 1 percent below the result of this investigation.

(b) Uranium Trichloride

The specific heat of a sample of unknown purity has been determined from low temperatures to 107° C by W. J. Ferguson and J. L. Prather [16] at the National Bureau of Standards. They give $C_p=0.0713$ cal g^{-1} deg^{-1} C at 0° C, which is 1 percent higher than the result of the present investigation. They report $C_p=103$ cal $mole^{-1}$ deg^{-1} C (equivalent to 0.0715 cal g^{-1} deg^{-1} C) for all temperatures from 17° to 107° C. This result is identical with those of this investigation from 53° to 107° C within the uncertainty of the number 103, or 0.5 percent. Correspondingly, the mean specific heat between 0° and 100° C is calculated to be 0.07147 cal g^{-1} deg^{-1} C, or 0.5 percent higher than the result of this investigation.

(c) Uranium Tetrachloride

The specific heat of a sample of unspecified purity has been determined from low temperatures to 82°C by W. J. Ferguson, J. L. Prather, and R. B. Scott.[17] Their results above 0°C are 0.3 to 0.6 percent higher than those of this investigation.

The experiments at 211.3° and 221.8°C in this investigation were performed with the intent of disclosing the second-order transition reported found at 211° by N. W. Gregory.[18] Such a transition would appear as a sudden change in slope of the plot of mean specific heat versus temperature. The deviations of the results at these temperatures from the function chosen to represent the data were, indeed, much larger than for the other results (see table 1). However, in view of the facts that only two experiments with the sample were made at each of these temperatures, and that values for blank experiments were obtained by interpolation rather than by direct measurement, it appears that the deviations (0.11 and 0.23 percent, respectively) of these results from the curve are not significantly greater than experimental error would allow. It can only be concluded that if this transition exists, it is quite small and occurs above 222°C for a pure sample.

[11] Classified report submitted to the Manhattan District, U. S. Army Corps of Engineers.
[12] See footnote 7.
[13] See footnote 11.
[14] See footnote 10.
[15] A. Blumcke, Ann. Physik, (III) **24**, 263 (1885).
[16] Classified report submitted to the Manhattan District, U. S. Army Corps of Engineers.
[17] See footnote 16.
[18] See footnote 16.

VI. Summary

The enthalpies of uranium, UCl_3 and UCl_4 at high temperatures have been determined. Values of specific heat and entropy have been derived. Values of the heats of transition of two first-order transformations in uranium are given. No evidence was found of first- or second-order transitions in UCl_3 or UCl_4.

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Specific Heat, Enthalpy, and Entropy of Uranyl Fluoride[1,2]

By Paul F. Wacker and Ruth K. Cheney

The heat capacity of uranyl fluoride was measured from 13° to 418° K by using a vacuum-type calorimeter equipped with thermostated radiation shields. From the data so obtained, the enthalpy $H^\circ - H_0^\circ$ was calculated to be 63.96, 77.62, and 108.15 int. joules per gram at 298.16°, 338.16°, and 423.16° K, respectively, and the entropy was calculated to be 0.4400, 0.4830, and 0.5635 int. joules per degree-gram at the same temperatures. No evidence of a transition was found. The values of the specific heat, enthalpy, entropy, and free energy are tabulated at 5-degree intervals of temperature.

I. Introduction

This investigation of the thermodynamic properties of uranyl fluoride was undertaken in connection with the Manhattan project and is a part of the program carried on during the war by the Heat and Power Division of the National Bureau of Standards.

II. Material

The uranyl fluoride used in this investigation was prepared by H. F. Priest of Columbia University. The material, after being dried at 130°C for 4 hours, was placed in the sample container. Air was removed by pumping until a high vacuum was obtained, helium was admitted at a pressure of 20 mm Hg, and the container was sealed with solder. The helium was added to promote the rapid attainment of thermal equilibrium. The observed heat capacity was adjusted for the presence of this helium.

Before the material was used in the calorimeter, an analysis made by the SAM Laboratories of the Carbide and Carbon Chemicals Corporation showed the sample to contain 77.19 weight percent of uranium and 12.6 weight percent of fluorine. Following the calorimetric measurements, the Uranium Section of the National Bureau of Standards found the sample to contain 77.28 percent of uranium and 12.1 percent of fluorine. The theoretical percentages are 77.28 and 12.33. Spectroscopic tests for 34 elements showed less than 0.07 weight percent impurity. The difficulties in fluorine analysis are such that it is probably improper to base any conclusions regarding purity of the sample on observed fluorine content.

III. Apparatus and Procedure

The calorimeter used in this investigation was of the adiabatic, vacuum type described by Southard and Brickwedde [1][3]. The sample container was the one used in the determination of the heat capacities of GR-S rubber [2] and polyvinyl chloride [3].

The system, including the measuring circuits, was very similar to that used by Scott, Meyers, Rands, Brickwedde, and Bekkedahl [4] to determine the heat capacity of butadiene, except for the following: The apparatus was designed for measuring the heat capacities of solids and so had no filling tube or attendant parts. The shield was suspended by means of fine wire, and the sample container was in turn suspended from the shield by means of linen cord. A copper, rather than an aluminum, shield was used on the bottom of the sample container to prevent heat losses from the exposed ends of the heater. The sample-

[1] This document is based on work performed for the Atomic Energy Project, and the information contained therein will appear in Division VIII of the National Nuclear Energy Series (Manhattan Project Technical Section) as part of the contribution of the National Bureau of Standards.

[2] Presented before the September 15, 1947, meeting of the American Chemical Society.

[3] Figures in brackets indicate the literature references at the end of this paper.

container heater was located in the thermometer well, which was filled with lead-tin eutectic solder. The side and bottom shield heaters were controlled individually. In order to improve the ease of controlling the radiation shields at temperatures above the ice point, an auxiliary heater was wrapped on the outer wall of the vacuum chamber, and the chamber was surrounded by a stirred oil bath. The auxiliary heater was used to keep this wall at a temperature only slightly below that of the shields and sample container. Its use resulted in a substantial improvement in shield control. Temperatures were measured with platinum resistance thermometer L15 (thermometer P), whose calibration is described in reference [5].

The methods of measurement and of calculation were similar to those described in the paper on butadiene [4]. The tare-heat capacity measurements were made on the empty sample container, and the gross-heat capacity measurements were made with 58.015_8 grams of uranyl fluoride in the container. Because of the negligible vapor pressure of the material, it was unnecessary to correct the heat capacities for vaporization. Specific heat measurements were regularly made with both high and low heating rates, the rates varying as much as from 0.63 to 2.18 degrees per minute. This procedure provided a test for a large proportion of the errors that might occur in the measurement of heat capacity, but would not have revealed an error whose magnitude per unit time was proportional to the heating rate.

IV. Calculations and Results

The observed heat capacity data were plotted as deviations from empirical equations. From the resulting deviation curves, values were read at uniform temperature intervals, and tables were constructed giving both the gross- and tare-heat capacities at 2.5-degree intervals below 115° K and at 5-degree intervals at higher temperatures. Subtraction of the tare- from the gross-heat capacity gave the net heat capacity, which was extrapolated to 0° K by means of the Debye equation $C=0.8359\ D\ (117/T)$. This equation represented the experimental data satisfactorily at 20°, 25°, and 30° K.

Due to graphical methods involved in getting the table of net-heat capacities, small irregularities could be detected in the higher differences. To reduce these, an analytical smoothing process was applied. The smoothed value corresponding to a given unsmoothed value was found by multiplying the unsmoothed value and the four adjacent unsmoothed values on either side of it by a set of coefficients. A number of such smoothing processes have been devised. The one adopted in the present work was developed by Harold W. Woolley. In it the coefficients were chosen to minimize the squares of the random parts of the first differences

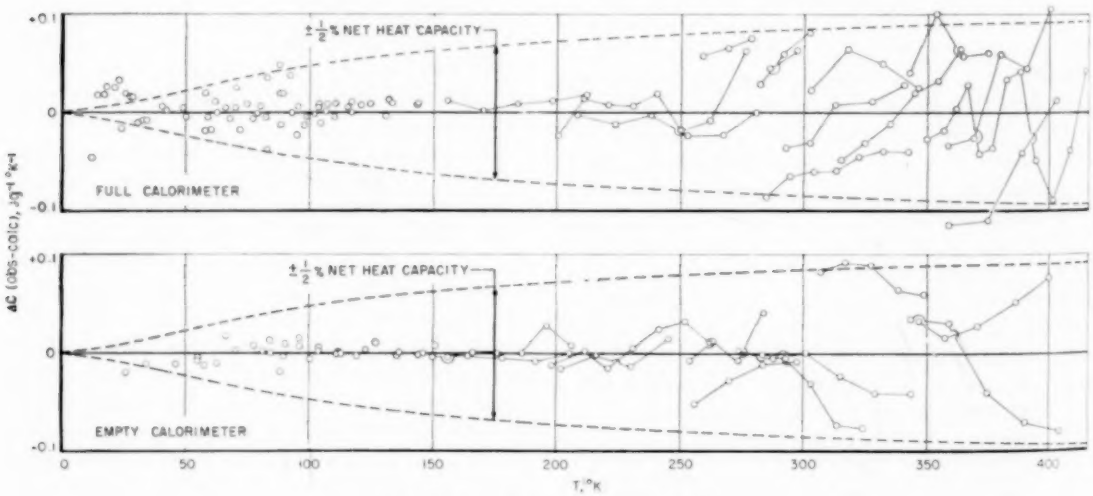

FIGURE 1. *Observed heat capacities.*

The dashed lines indicate deviations from the tables of gross and tare heat capacities equal to ±0.5 percent of the net heat capacity.

in such a manner that the process would make no significant change in functions for which the fourth and higher differences were negligible. The smoothing operation introduced no changes in the table as large as the probable experimental error.

The enthalpy was calculated from the formula $H^\circ = \int C^\circ dT$, while the entropy was obtained from the equation $S^\circ = \int (C^\circ/T) dT$. The free energy was calculated from the relation $F^\circ = -\int S^\circ dT$ and also from the relation $F^\circ = H^\circ - TS^\circ$. This provided a check on the accuracy of the integrations. Simpson's rule was used at the higher temperatures. Between 20° and 115°K, a tabular integration formula involving four rather than three successive tabular entries was used, and below 20°, the integrals were obtained directly from the Debye equation. The results are presented in table 1. The dashed lines in figure 1, representing 0.5 percent of the heat capacity, show the temperature trend of the specific heat.

TABLE 1.—*Heat capacity, enthalpy, entropy, and free energy of uranyl fluoride*

T	C°	$H^\circ - H_0^\circ$	S°	$-(F^\circ - H_0^\circ)$	T	C°	$H^\circ - H_0^\circ$	S°	$-(F^\circ - H_0^\circ)$
(°K)	(Int. j/g) °K⁻¹	Int. j/g	(Int. j/g) °K⁻¹	Int. j/g	(°K)	(Int. j/g) °K⁻¹	Int. j/g	(Int. j/g) °K⁻¹	Int. j/g
0	0.00000	0.00000	0.00000	0.00000	215	0.2949	37.626	0.33987	34.802
5	.00051	.00064	.00017	.00021	220	.2979	39.107	.34368	36.503
10	.00403	.01014	.00135	.00339	225	.3008	40.604	.34741	38.238
15	.01231	.0492	.00440	.01690	230	.3037	42.116	.35705	40.006
20	.02333	.1378	.00943	.0508	235	.3064	43.641	.36361	41.808
25	.03386	.2803	.01575	.1133	240	.3090	45.179	.37009	43.643
30	.04478	.4768	.02288	.2096	245	.3116	46.731	.37649	45.518
35	.05567	.7280	.03060	.3431	250	.3142	48.295	.38281	47.400
40	.06637	1.0331	.03874	.5163	255	.3166	49.872	.38905	49.337
45	.07747	1.3925	.04719	.7310	260	.3190	51.462	.39523	51.298
50	.08909	1.8086	.05595	.9887	265	.3214	53.063	.40133	53.290
55	.10191	2.2855	.06503	1.2910	270	.3237	54.676	.40735	55.310
60	.11549	2.8292	.07448	1.6396	275	.3259	56.300	.41331	57.362
65	.12713	3.4371	.08420	2.0363	280	.3280	57.934	.41920	59.443
70	.13573	4.0951	.09395	2.4817	285	.3300	59.579	.42503	61.555
75	.14362	4.7933	.10358	2.9756	290	.3320	61.235	.43079	63.694
80	.15261	5.5333	.11313	3.5174	295	.3339	62.900	.43648	65.862
85	.16310	6.3220	.12269	4.1070	300	.3357	64.574	.44210	68.058
90	.17378	7.1647	.13232	4.7443	305	.3374	66.256	.44767	70.284
95	.18226	8.0560	.14196	5.4302	310	.3390	67.947	.45317	72.536
100	.18847	8.9834	.15147	6.1638	315	.3406	69.647	.45860	74.814
105	.19439	9.9404	.16081	6.9446	320	.3422	71.354	.46398	77.121
110	.2007	10.928	.16999	7.7713	325	.3438	73.069	.46930	79.454
115	.2070	11.947	.17905	8.6443	330	.3454	74.792	.47456	81.814
120	.2132	12.998	.18800	9.5620	335	.3470	76.523	.47976	84.199
125	.2193	14.079	.19682	10.524	340	.3486	78.262	.48492	86.612
130	.2252	15.190	.20554	11.530	345	.3502	80.009	.49002	89.049
135	.2308	16.331	.21415	12.579	350	.3517	81.764	.49507	91.512
140	.2362	17.498	.22264	13.671	355	.3532	83.526	.50007	94.000
145	.2413	18.692	.23102	14.806	360	.3546	85.296	.50502	96.512
150	.2463	19.911	.23928	15.981	365	.3560	87.072	.50992	99.050
155	.2510	21.154	.24743	17.198	370	.3572	88.855	.51477	101.611
160	.2556	22.421	.25547	18.455	375	.3584	90.645	.51957	104.197
165	.2598	23.710	.26340	19.752	380	.3596	92.440	.52433	106.806
170	.2640	25.019	.27122	21.089	385	.3607	94.241	.52904	109.440
175	.2679	26.349	.27893	22.464	390	.3617	96.046	.53370	112.098
180	.2717	27.698	.28653	23.878	395	.3627	97.858	.53831	114.776
185	.2753	29.066	.29403	25.330	400	.3638	99.674	.54288	117.480
190	.2788	30.451	.30141	26.818	405	.3648	101.495	.54741	120.206
195	.2822	31.854	.30870	28.343	400	.3658	103.321	.55189	122.954
200	.2854	33.273	.31589	29.906	415	.3668	105.153	.55633	125.725
205	.2886	34.708	.32297	31.502	420	.3678	106.989	.56073	128.518
210	.2917	36.159	.32997	33.135	425	.3688	108.831	.56508	131.330

V. Discussion

Although tests were made for transitions, none were found.

The probable error in the tabulated values of the specific heat of the sample used in this investigation is estimated to be 0.1 percent from 40° to 250° K. Below 40° K the error is larger, perhaps reaching 1 percent at 20° K. As radiation becomes an important source of error above room temperature, the probable error above 250° K may become as large as 0.5 percent. These estimates do not include errors due to impurities in the sample. Although there is probably no reliable evidence for more than 0.07 weight percent impurity in the sample, the lack of detailed knowledge of the purity does introduce some uncertainty in the results.

VI. References

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Purification, Purity, and Freezing Points of *n*-Decane, 4 Alkylcyclopentanes, 9 Alkylcyclohexanes, 2 Monoolefins, 1, 2-Butadiene, and 2-Butyne of the API-Standard and API-NBS Series[1*]

By Anton J. Streiff[2], Evelyn T. Murphy,[2] Janice C. Zimmerman,[2] Laurel F. Soule,[2] Vincent A. Sedlak,[2] Charles B. Willingham, and Frederick D. Rossini

This report describes the purification and determination of freezing points and purity of 18 hydrocarbons of the API-Standard and API-NBS series, including one paraffin, four alkylcyclopentanes, nine alkylcyclohexanes, two monoolefins, one diolefin, and one acetylene.

I. Introduction

Previous reports described the purification and determination of freezing points and purity of 66 hydrocarbon compounds of the API-Standard and API-NBS series, which were produced as part of the cooperative program on standard samples of hydrocarbons of the National Bureau of Standards and the American Petroleum Institute [1, 2, 3].[3] This report describes the purification and determination of freezing points and purity of an additional 18 hydrocarbon compounds under this cooperative program, including *n*-decane, 4 alkylcyclopentanes, 9 alkylcyclohexanes, 2 monoolefins, 1,2-butadiene and 2-butyne.

The final lots of the material labeled API-Standard are sealed "in vacuum" in glass ampoules and made available as NBS standard samples of hydrocarbons, by the American Petroleum Institute and the National Bureau of Standards. The material labeled API-NBS is made available in appropriate small lots, through the American Petroleum Institute Research Project 44 at the National Bureau of Standards, on loan to qualified investigators for the measurement of needed properties.

II. Materials

The starting materials were supplied as follows:

By the API Research Project 45 on the "Synthesis and Properties of Hydrocarbons of Low-Molecular Weight" at the Ohio State University, Columbus, Ohio, under the supervision of C. E. Boord:

Isobutylcyclopentane.
cis-1,3-Dimethylcyclohexane.
trans-1,3-Dimethylcyclohexane.
n-Propylcyclohexane.
Isopropylcyclohexane.
1,1,3-Trimethylcyclohexane.
n-Butylcyclohexane.
Isobutylcyclohexane.
sec-Butylcyclohexane.
tert-Butylcyclohexane.
2-Butyne.

By the Hydrocarbon Laboratory at the Pennsylvania State College, State College, Pa., under the supervision of F. C. Whitmore:

1-Methyl-1-ethylcyclopentane.
cis-1-Methyl-2-ethylcyclopentane.
3,3-Dimethyl-1-butene.

By the Standard Oil Development Co., Esso Laboratories, Elizabeth, N. J., and Baton Rouge, La., through W. J. Sweeney:

1,2-Butadiene.

By the Tide Water Associated Oil Co., Associated, Calif., through H. Y. Hyde:

Cyclopentane (B) [4]

By the API Research Project 6 at the National Bureau of Standards, through F. D. Rossini:

n-Decane.
1-Octene.

[1] This investigation was performed at the National Bureau of Standards as part of the work of the American Petroleum Institute Research Project 6 on the Analysis, Purification, and Properties of Hydrocarbons.

[*] Presented before the Division of Petroleum Chemistry of the American Chemical Society at the meeting in New York, September 1947.

[2] Research Associate on the American Petroleum Institute Research Project 6 at the National Bureau of Standards.

[3] Figures in brackets indicate the literature references at the end of this paper.

[4] See footnote "a" of table 2.

TABLE 1.—*Information on the purification of 18 API-Standard and API-NBS hydrocarbons*

Compound[a]	Starting material provided by	Hydrocarbon charged for distillation		Distillation[f]								Volume of selected sample	
				Kind[c]	Azeotrope-forming substance[d]	Amount of hydrocarbon in the azeotropic distillate[e]	Distilling column number	Number of theoretical plates (approx.)	Reflux ratio (approx.)	Rate of collection of distillate	Results plotted in figure	API-Standard	API-NBS
	laboratory[b]	Volume	Purity			percentage by volume				ml/hour		ml	ml
Paraffins													
n-Decane	API RP 6[g]	[h]5.80	9855±006	Reg.			14	125	125/1	12.5	1		
		[i]5.80	9984±002	Reg.			7	130	145/1	8.5	2	1400	415
Alkylcyclopentanes													
Cyclopentane (B)	Tide Water Assoc.	2.45	9984±002	Reg.			2	100	150/1	2.0	3	1020	300
1-Methyl-1-ethylcyclopentane	Penn State	2.10		Azeo.	Ethanol	33	4	200	180/1	4.0	4	1240	370
cis-1-Methyl-2-ethylcyclopentane	Penn State	1.73	94.0±0.5	Azeo.	Isopropanol	14	4	200	180/1	4.0	5	716	158
Isobutylcyclopentane	API RP 45	3.19		Reg.			13	130	155/1	8.0	6		
		2.25	9982±008	Azeo.	Cell.	59	10	135	165/1	4.5	7	1060	290
Alkylcyclohexanes													
cis-1,3-Dimethylcyclohexane[j]	API RP 45	[l]5.90		Reg.			15	125	125/1	12.5	8		
		[m]5.98		Reg.			7	130	145/1	8.5	9		
		2.60	9989±005	Azeo.	Me. Cell.	66	15A	200	160/1	4.5	10	1200	360
trans-1,3-Dimethylcyclohexane[k]	API RP 45	[l]5.90		Reg.			15	125	125/1	12.5	8		
		[m]3.00		Azeo.	Ethanol	35	9	135	165/1	4.5	11	1100	360
n-Propylcyclohexane	API RP 45	1.48		Reg.			8	130	145/1	8.5	12		
		[n]1.05		Azeo.	Cell.	40	9	135	165/1	4.5	13	365	[p]
		[o]2.25	9948±008	Azeo.	Cell.	40	9	135	165/1	4.5	14	895	360
Isopropylcyclohexane	API RP 45	3.90		Reg.			8	130	155/1	8.0	15		
		1.79	98.8±0.1	Azeo.	Cell.	43	10	135	165/1	4.5	16	875	147
1,1,3-Trimethylcyclohexane	API RP 45	2.72		Reg.			7	130	155/1	8.0	17		
		1.80	9964±008	Azeo.	Me. Cell.	63	10	135	165/1	4.5	18	905	193
n-Butylcyclohexane	API RP 45	2.50		Reg.			13	130	155/1	8.0	19		
		1.71	9987±008	Azeo.	Butyl Cell.	52	10	135	165/1	4.5	20	870	25
Isobutylcyclohexane	API RP 45	1.91		Reg.			2	100	150/1	2.0	21		
		1.53	9975±009	Azeo.	Butyl Cell.	63	11A	200	160/1	4.5	22	930	185
sec-Butylcyclohexane	API RP 45	2.59		Reg.			12	135	165/1	4.5	23		
		2.13		Azeo.	Butyl Cell.	54	11A	200	160/1	4.5	24	975	210
tert-Butylcyclohexane	API RP 45	2.53		Reg.			12	135	165/1	4.5	25		
		1.68	9994±003	Azeo.	Cell.	26	8	130	145/1	8.5	26	1135	285
Olefins													
3,3-Dimethyl-1-butene	Penn State	3.80	9886±015	Reg.			9	135	165/1	4.5	27	1300	385
1-Octene	API RP 6[g]	[q]6.00		Reg.			13	130	155/1	8.0	28		
		[r]6.15	9970±013	Reg.			13	130	155/1	8.0	29	2000	600
Diolefins													
1,2-Butadiene	Std. Oil Dev.	1.40		Reg.			1	150	150/1	2.0	30		
		1.00		Reg.			1	150	150/1	2.0	31	600	100
Acetylenes													
2-Butyne	API RP 45	2.68		Reg.			1	150	150/1	2.0	32	1125	265

See footnotes on page 324.

Table 1 summarizes the amounts of the starting materials and gives some additional information as to the source and purity.

III. Purification

The procedure followed in the process of purification and determination of purity was the same as that described in the previous reports [2, 3].

In addition to the name of the laboratory supplying the starting materials, table 1 and its footnotes give complete information for each distillation for each of the compounds.

Details of the distillation apparatus and operations are described in reference [5].

Figures 1 to 32, inclusive, show graphically the results of the distillations listed in table 1. These figures give, as a function of volume of hydrocarbon distillate, the refractive index (n_D at 25° C, to ±0.0001), the boiling point of the distillate (at the controlled pressure of 724.5 mm Hg, to ±0.01° C), the freezing point of selected fractions of hydrocarbon distillate (in air at 1 atm usually with a precision near ±0.003° C), and the purity of the hydrocarbon distillate. The letters *W*, *X*, *Y*, *Z* indicate the disposition of the material, as follow: *W*, returned to the laboratory supplying the material; *X*, blended for redistillation; *Y*, used for the API-Standard material; *Z*, used for the API-NBS material.

Footnotes for Table 1, Page 322.

[a] See footnote "a" of table 2.

[b] The abbreviations represent the following laboratories:
APIRP45; American Petroleum Institute Research Project 45 at the Ohio State University, Columbus, Ohio.
Penn State; Hydrocarbon Laboratory at the Pennsylvania State College, State College, Pa.
Std. Oil Dev.; Standard Oil Development Co. Esso Laboratories, Elizabeth, N. J. and Baton Rouge, La.
Tide Water Assoc.; Tide Water Associated Oil Co., Associated, Calif.
APIRP6; American Petroleum Institute Research Project 6 at the National Bureau of Standards, Washington 25, D. C.

[c] The abbreviations are: Azeo., azeotropic; Reg., regular.

[d] The abbreviations are: Cell., Cellosolve (ethylene glycol monoethyl ether); me. Cell., methyl Cellosolve (ethylene glycol monomethyl ether); Butyl Cell., butyl Cellosolve (ethylene glycol monobutyl ether).

[e] Approximate value obtained from the actual volume of hydrocarbon recovered by extracting the azeotrope-forming substance with water in separatory funnels.

[f] See reference [5] for further details.

[g] Obtained by purchase of commercially available material from the Connecticut Hard Rubber Co., New Haven, Conn.

[h] One of two similar charges.

[i] This charge consisted of material, having substantially the same composition, from each of the two previous distillations (see footnote "h").

[j] See footnote "f" of table 2.

[k] See footnote "g" of table 2.

[l] One of three charges of similar material, two of which were 5.90 liters each, and the third of which was 2.50 liters. Both *cis* and *trans-1,3*-dimethylcyclohexane were obtained from this material (see fig. 8).

[m] This charge consisted of material, having substantially the same composition, from each of the three previous distillations (see footnote "l").

[n] The 1.05 liters for this charge consisted of 0.93 liter from the first distillation in column 8 (see fig. 12), and 0.12 liter which was a second lot of *n*-propylcyclohexane supplied by the API Research Project 45.

[o] This is a third lot of *n*-propylcyclohexane supplied by the API Research Project 45.

[p] Total volume of the API-Standard sample was 1,260 ml.

[q] One of two charges of similar material, the second of which was 6.28 liters.

[r] This charge consisted of material, having substantially the same composition, from each of the two previous distillations (see footnote "q").

As demonstrated in the previous reports [2, 3], the blending of fractions of distillate for the preparation of material of the highest purity can be done safely only on the basis of freezing points of selected fractions.

IV. Freezing Points, Cryoscopic Constants, and Purity

Table 2 gives the following information for each of the 18 compounds, except as otherwise indicated: The kind of time-temperature curves, whether freezing or melting, used to determine the freezing point [6]; the freezing point of the actual sample, in air at 1 atm [6], for both the API–Standard and API-NBS lots; the calculated value of the freezing point for zero impurity [6]; the value of the cryoscopic constant, determined from the lowering of the freezing point on the addition of a known amount of an appropriate impurity [6]; and the resulting calculated amount of impurity in the API-Standard and the API-NBS material.

Grateful acknowledgment is made to the other organizations and individuals listed in section II of this report for their contributions of materia for use in this work.

V. References

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[6] A. R. Glasgow, Jr., A. J. Streiff, and F. D. Rossini, Research NBS **35,** 355 (1945) RP1676.

[7] American Petroleum Institute Research Project 44 a the National Bureau of Standards. Selected valu of properties of hydrocarbons. Tables 1z, 2z, 3 5z, 6z, 7z, and 8z.

[8] American Petroleum Institute Research Project 41 a the National Bureau of Standards. Selected Valu of Properties of Hydrocarbons. Table 7a.

TABLE 2.—*Freezing points and purity of 18 API-Standard and API-NBS hydrocarbons*

Compound[a]	Kind of time-temperature observations used to determine the freezing point[b]	Freezing point of the actual selected sample, in air at 1 atm[c]		Freezing point for zero impurity in air at 1 atm[c]	Cryoscopic constant[b] A	Calculated amount of impurity in the actual selected sample[d]	
		°C		°C	deg⁻¹	mole percent	
		API-Standard	API-NBS			API-Standard	API-NBS
Paraffins							
n-Decane	F	29.680	-29.677	-29.673 ±0.005	[e](0.0585)	0.04±0.02	0.023±0.018
Alkylcyclopentanes							
Cyclopentane (B)	F	-93.902	-93.887	-93.77 ±0.04	[e](0.00227)	0.030±0.009	0.026±0.009
1-Methyl-1-ethylcyclopentane	F and M	-143.83	-143.82	-143.800 ±0.018	0.0444	0.13±0.08	0.09±0.08
cis-1-Methyl-2-ethylcyclopentane	F and M	-106.05(I)	-106.01(I)	-105.95 ±0.05(I) -106.62 ±0.05(III)(u)	0.0480(I)	0.48±0.24	0.29±0.24
Isobutylcyclopentane	M	-115.264	-115.254	-115.225 ±0.020	0.0405	0.16 ±0.08	0.12±0.08
Alkylcyclohexanes							
cis-1,3-Dimethylcyclohexane[f]	M	-75.588	-75.579	-75.560 ±0.015	[e](0.0333)	0.09±0.05	0.06±0.05
trans-1,3-Dimethylcyclohexane[g]	M	-90.145	-90.134	-90.100 ±0.020	[e](0.035)	0.16 ±0.07	0.12 ±0.07
n-Propylcyclohexane	M	-94.924	-94.918	-94.900 ±0.015	0.0324	0.08±0.05	0.06 ±0.05
Isopropylcyclohexane	F and M	-89.432	-89.416	-89.390 ±0.020	0.0373	0.16 ±0.07	0.10 ±0.07
1,1,3-Trimethylcyclohexane	F and M	-65.831	-65.809	-65.750 ±0.020	0.0260	0.21±0.05	0.15 ±0.05
n-Butylcyclohexane	M	-74.747	-74.736	-74.725 ±0.010	0.0385	0.08±0.04	0.042±0.039
Isobutylcyclohexane	M	-94.839(I)	-94.830(I)	-94.78 ±0.03(I) -95.72 ±0.04(III)(u)	0.0291(I)	0.17 ±0.09	0.15 ±0.09
sec-Butylcyclohexane						[h](0.30±0.20)	[h](0.25±0.20)
tert-Butylcyclohexane	M	-41.173	-41.170	-41.158 ±0.010	0.0303	0.05±0.03	0.04±0.03
Olefins							
3,3-Dimethyl-1-butene	F and M	-115.370	-115.365	-115.20 ±0.12	[e](0.00530)	0.09±0.06	0.09±0.06
1-Octene	F and M	-101.748	-101.746	-101.710 ±0.020	0.0637	0.24±0.13	0.23±0.13
Diolefins							
1,2-Butadiene	M	-136.209	-136.204	-136.190 ±0.012	[e](0.04462)	0.08±0.05	0.06 ±0.05
Acetylenes							
2-Butyne	F and M	-32.296	-32.281	-32.260 ±0.020	[e](0.0191)	0.069±0.038	0.041±0.038

[a] (*B*) following the name of a compound indicates that for the API-NBS series, it is a second (and usually slightly purer) sample of the given compound, the first sample of which is labeled (*A*). See reference [4].

[b] *F* indicates freezing and *M* indicates melting. See reference [6] for experimental details and the definition of the cryoscopic constant.

[c] When a given hydrocarbon has more than one crystalline form, the several forms will be labeled I, II, and III, in order of decreasing temperature of fusion (or freezing point). Forms other than I will be, at their respective freezing points, in metastable equilibrium with the undercooled liquid, but will be unstable with respect to transition to some other solid form at the same temperature and pressure (1 atm). This is indicated by a letter *u* in parentheses following the Roman numeral.

[d] The values in this column, except as otherwise indicated, were calculated as described in reference [6], using the values of the cryoscopic constants and freezing points for zero impurity given in the preceding columns.

[e] Not determined in this investigation. From the "*z*" tables of the American Petroleum Institute Research Project 44 [7].

[f] This isomer, formerly labeled "*trans*", has the following properties: Boiling point at 1 atm, 120.09° C; refractive index, n_D at 25° C, 1.4206; density at 25° C, 0.7620 g/ml [8].

[g] This isomer, formerly labeled "*cis*", has the following properties: boiling point at 1 atm, 124.45° C; refractive index, n_D at 25° C, 1.4284; density at 25° C, 0.7806 g/ml [8].

[h] Estimated by analogy with isomers subjected to similar purification.

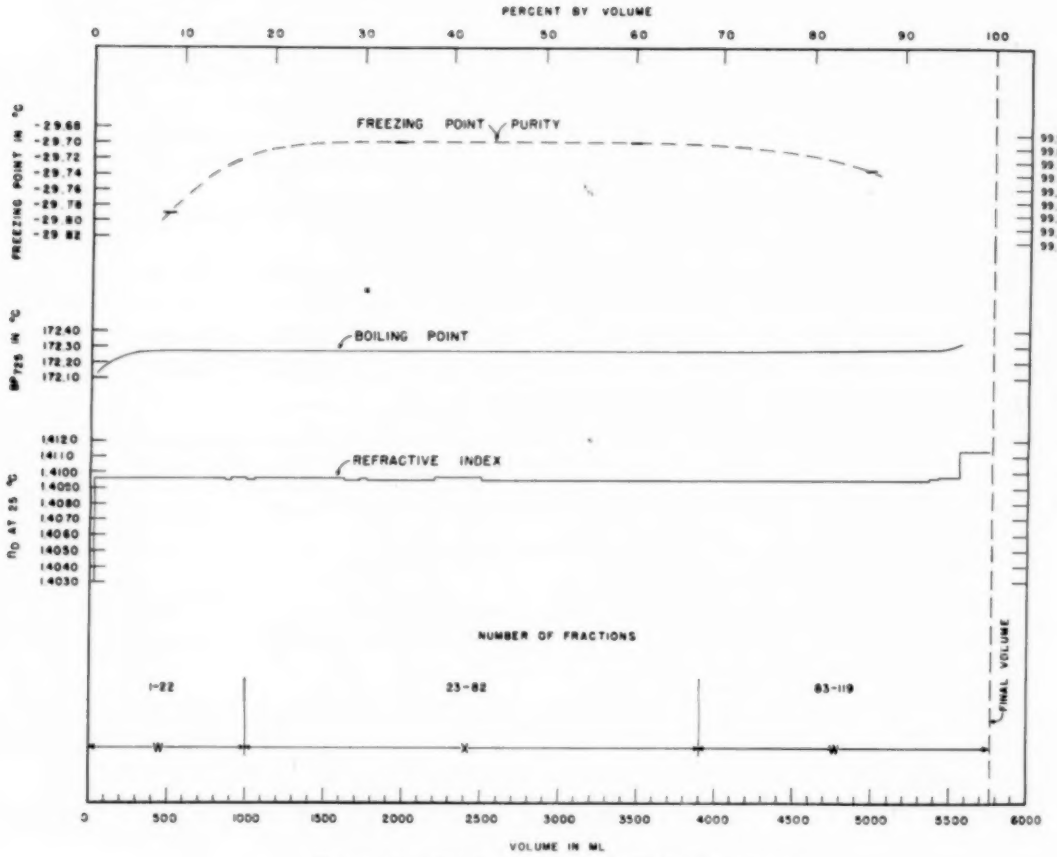

FIGURE 1.—*Results of the first distillation of n-decane.*

Regular distillation at 725 mm Hg in still 14 (7/27/45 to 8/18/45). This is one of two similar distillations.

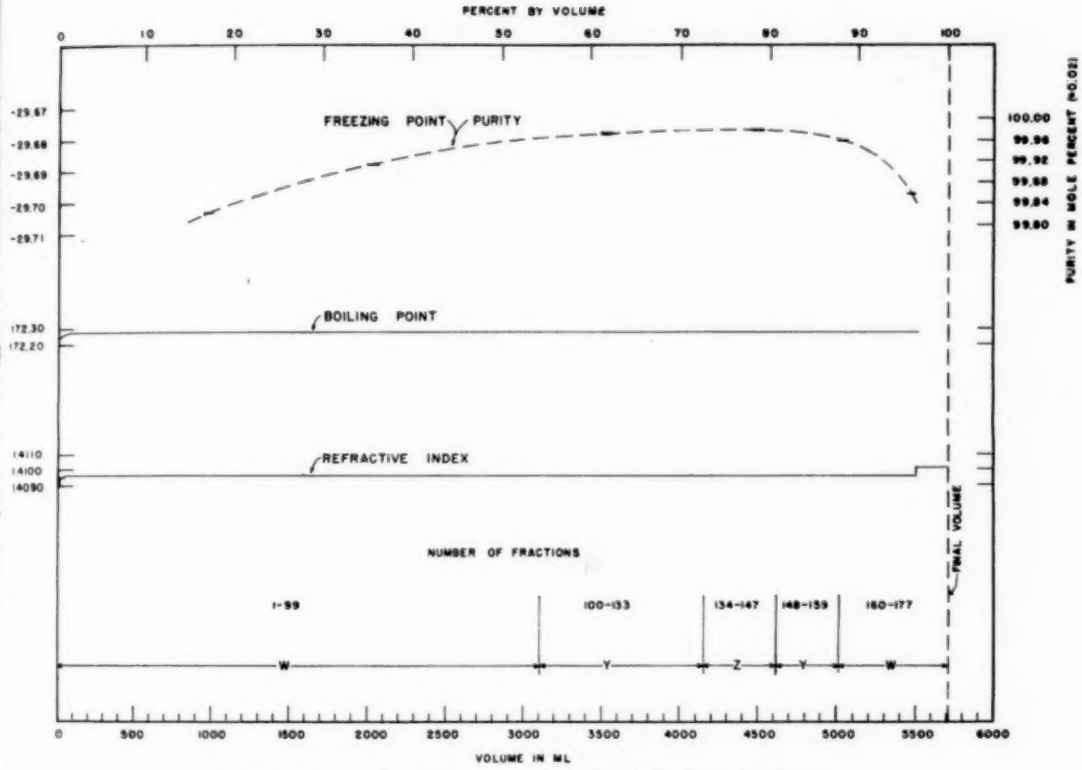

FIGURE 2.—*Results of the second and final distillation of n-decane.*

Regular distillation at 725 mm Hg in still 7 (9/18/45 to 10/22/45). See footnote "1" of table 1.

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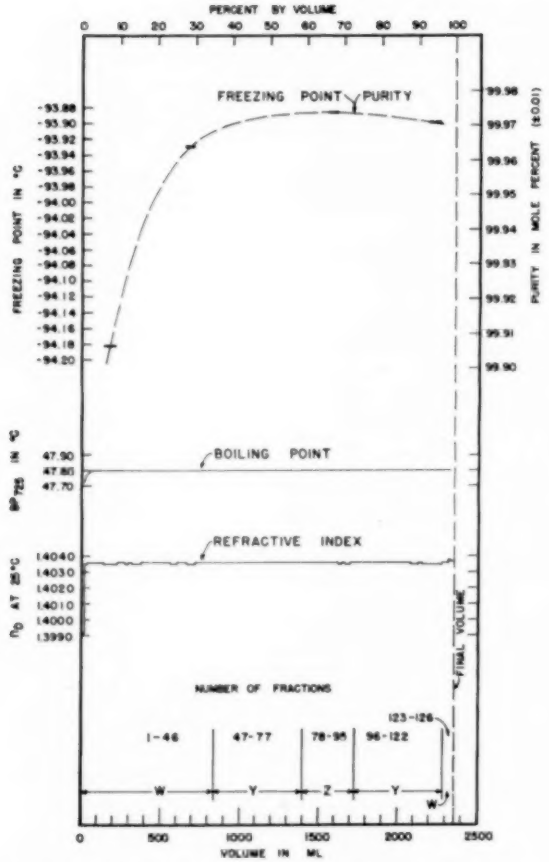

FIGURE 3.—*Results of the first and only distillation of cyclopentane.*

Regular distillation at 725 mm Hg in still 2 (1/29/46 to 3/25/46).

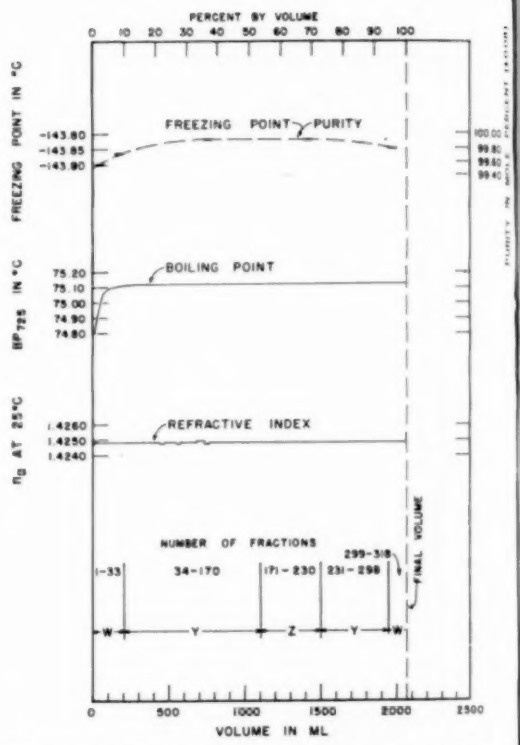

FIGURE 4.—*Results of the first and only distillation of 1-methyl-1-ethylcyclopentane.*

Azeotropic distillation with ethanol at 725 mm Hg in still 4 (2/25/46 to 4/22/46).

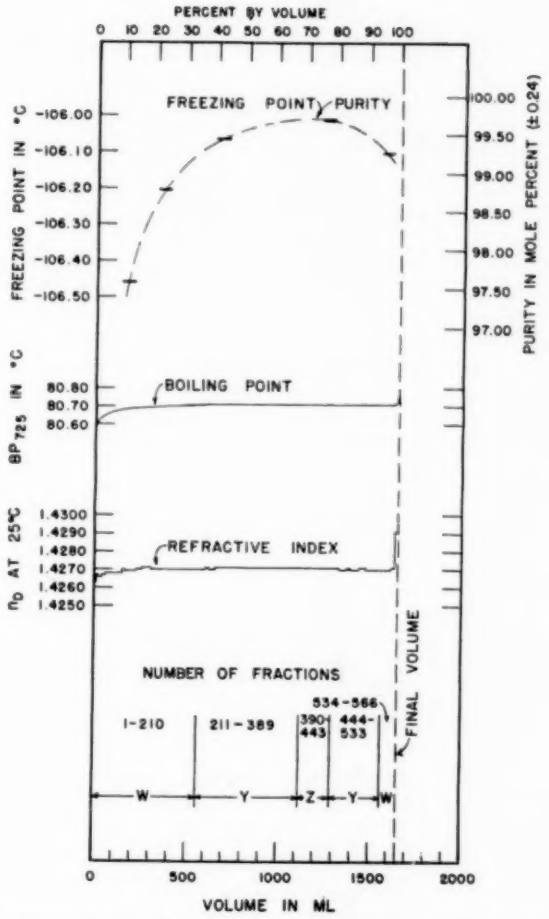

FIGURE 5.—*Results of the first and only distillation of cis-1-methyl-2-ethylcyclopentane.*

Azeotropic distillation with isopropanol at 725 mm Hg in still 4 (5/22/46 to 8/28/46).

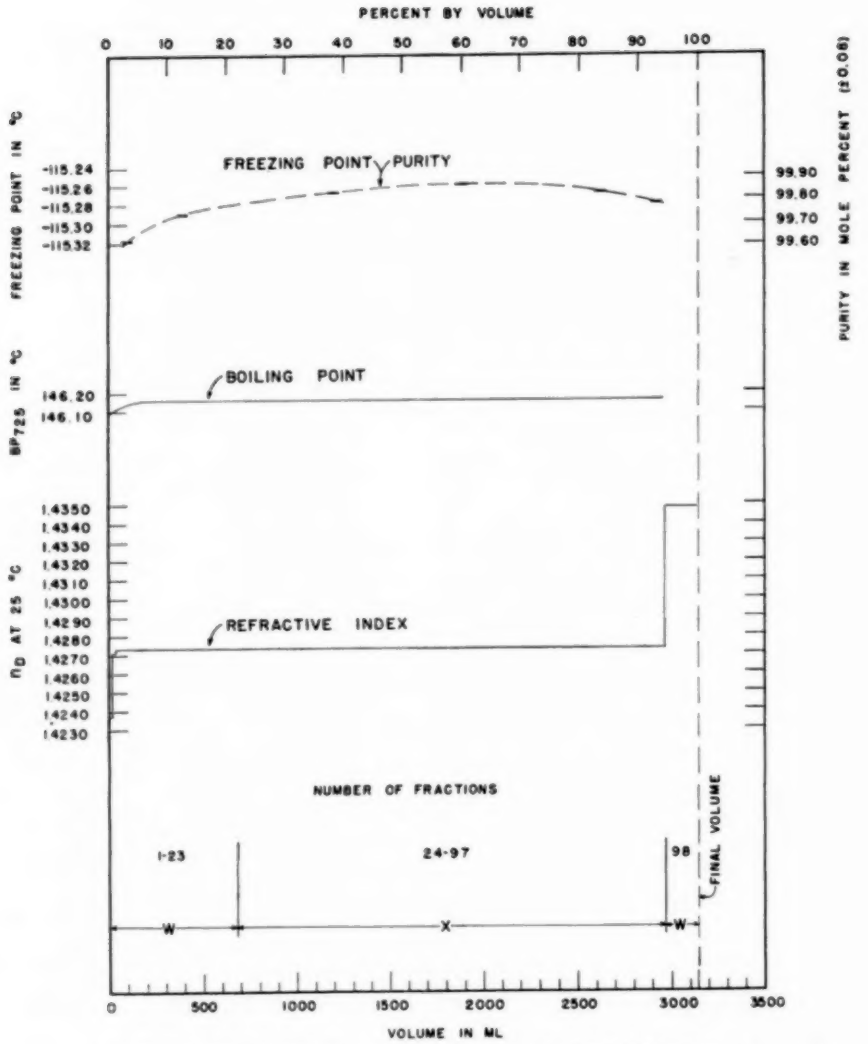

FIGURE 6.—*Results of the first distillation of isobutylcyclopentane.*

Regular distillation at 725 mm Hg in still 13 (12/7/45 to 12/28/45).

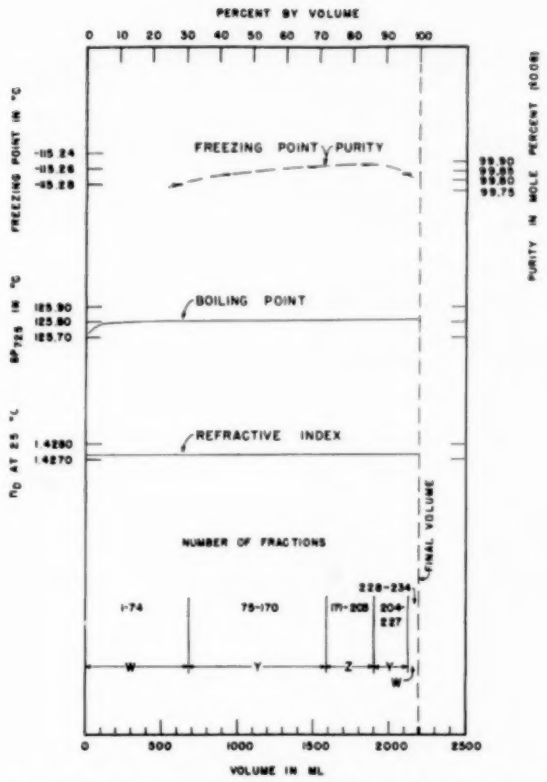

FIGURE 7.—*Results of the second and final distillation of isobutylcyclopentane.*

Azeotropic distillation with ethylene glycol monoethyl ether at 725 mm Hg in still 10 (9/3/46 to 10/14/46).

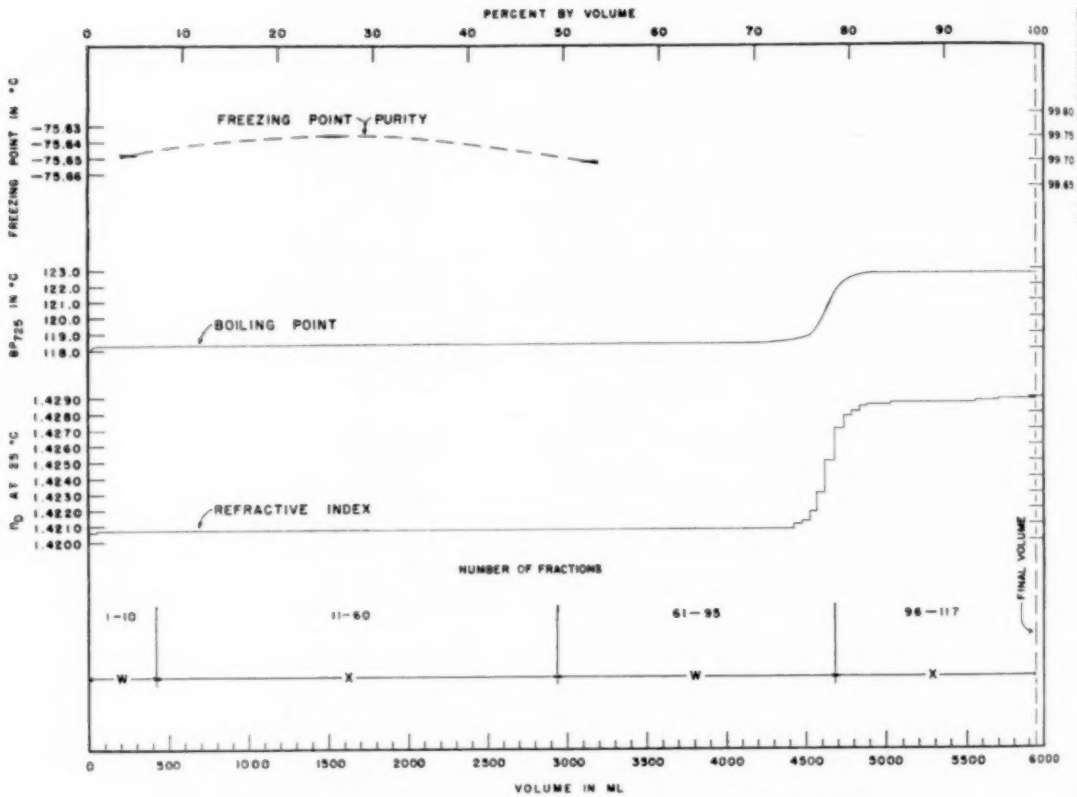

FIGURE 8.—*Results of the first distillation of cis and trans-1, 3-dimethylcyclohexane.*

Regular distillation at 725 mm Hg in still 15 (3/27/46 to 4/17/46). One of three distillations of similar material. See footnote "l" of table 1. Fractions 11 to 60 were redistilled to obtain *cis*-1,3-dimethylcyclohexane (see fig. 9 and footnote "f" of table 2). Fractions 96 to 117 were redistilled to obtain *trans*-1, 3-dimethylcyclohexane (see fig. 11 and footnote "g" of table 2).

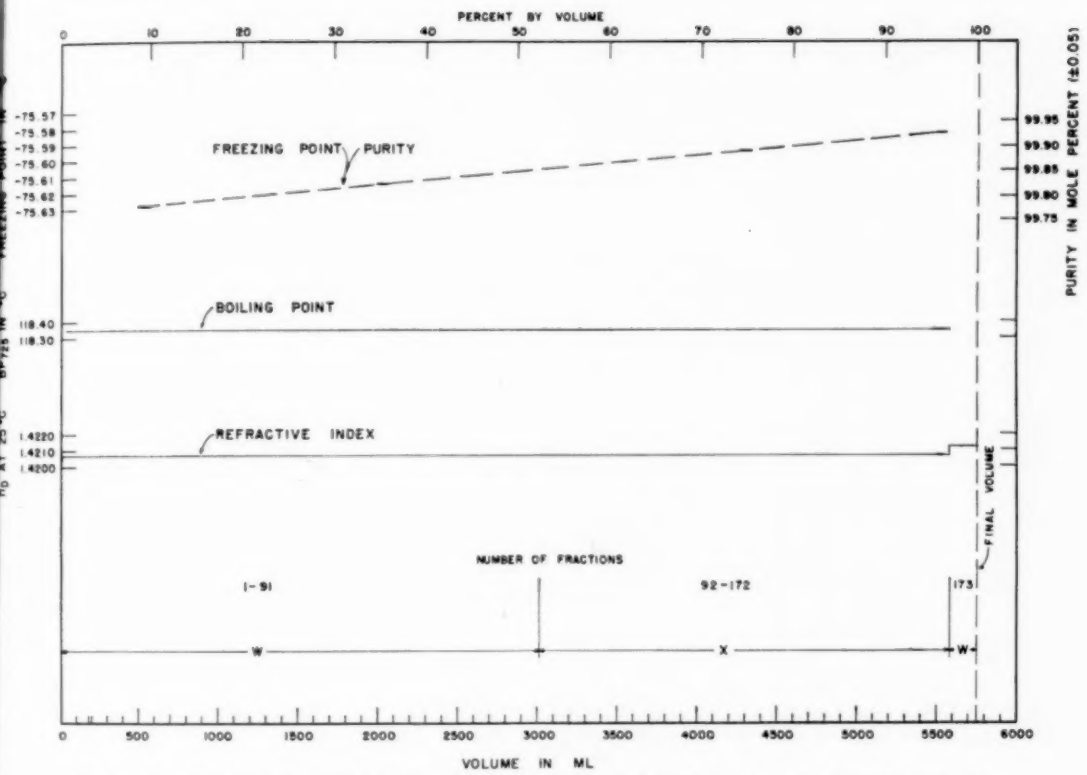

FIGURE 9.—*Results of the second distillation of cis-1,3-dimethylcyclohexane (see footnote "f" of table 2).*

Regular distillation at 725 mm Hg in still 7 (5/3/46 to 6/3/46).

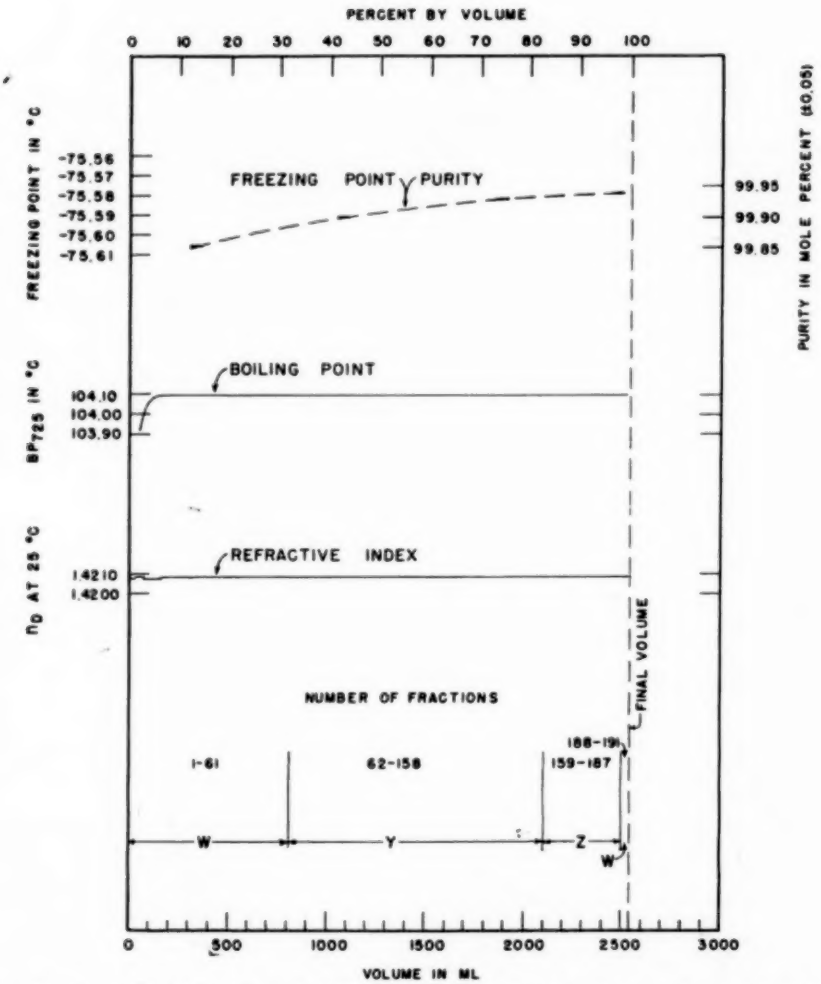

FIGURE 10.—*Results of the third and final distillation of cis-1,3-dimethylcyclohexane (see footnote "f" of table 2).*

Azeotropic distillation with ethylene glycol monomethyl ether at 725 mm Hg in still 15A (6/29/46 to 8/5/46).

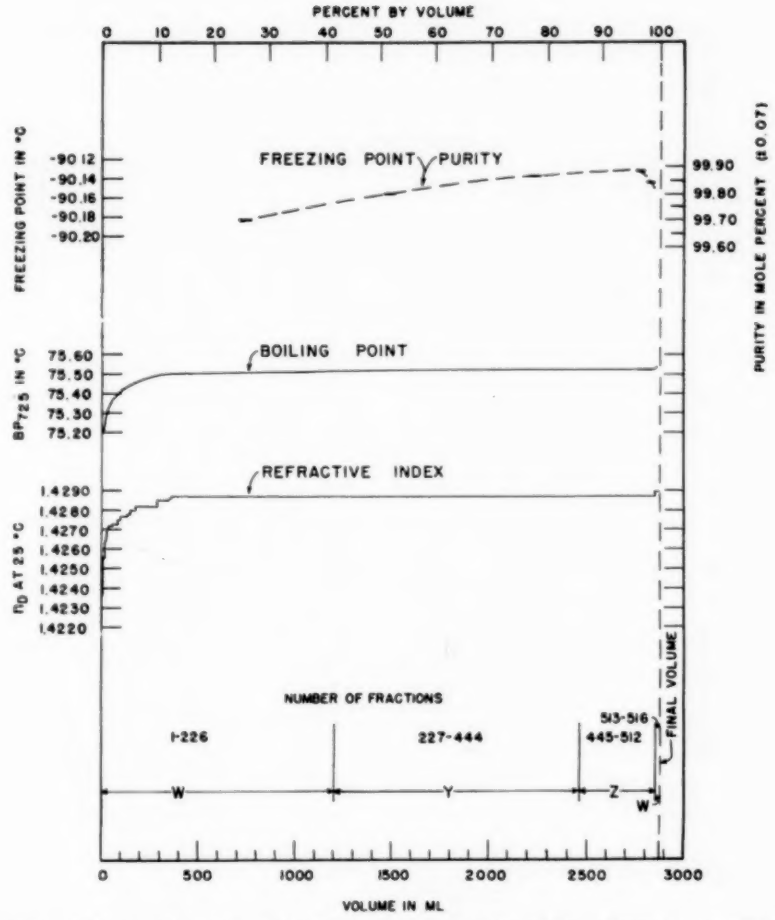

FIGURE 11.—*Results of the second and final distillation of trans-1,3-dimethylcyclohexane (see footnote "g" of table 2).*

Azeotropic distillation with ethanol at 725 mm Hg in still 9 (5/4/46 to 8/3/46).

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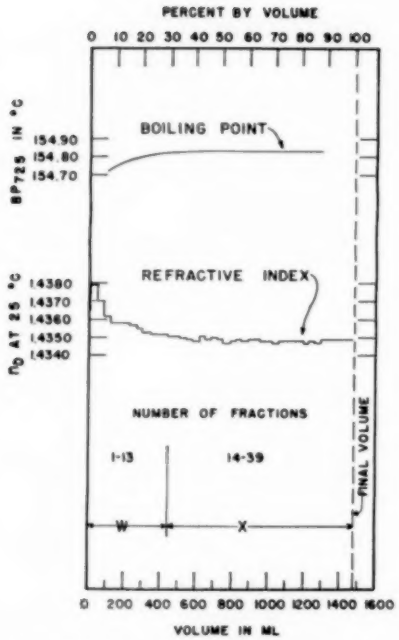

FIGURE 12.—*Results of the first distillation of n-propylcyclohexane.*

Regular distillation at 725 mm Hg in still 8 (5/5/44 to 5/11/44).

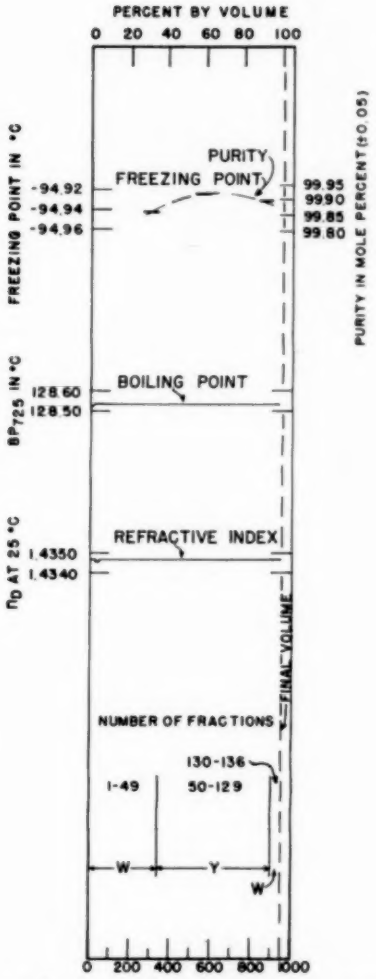

FIGURE 13.—*Results of the second distillation of n-propylcyclohexane.*

Azeotropic distillation with ethylene glycol monoethyl ether at 725 mm Hg in still 9 (6/14/44 to 7/10/44).

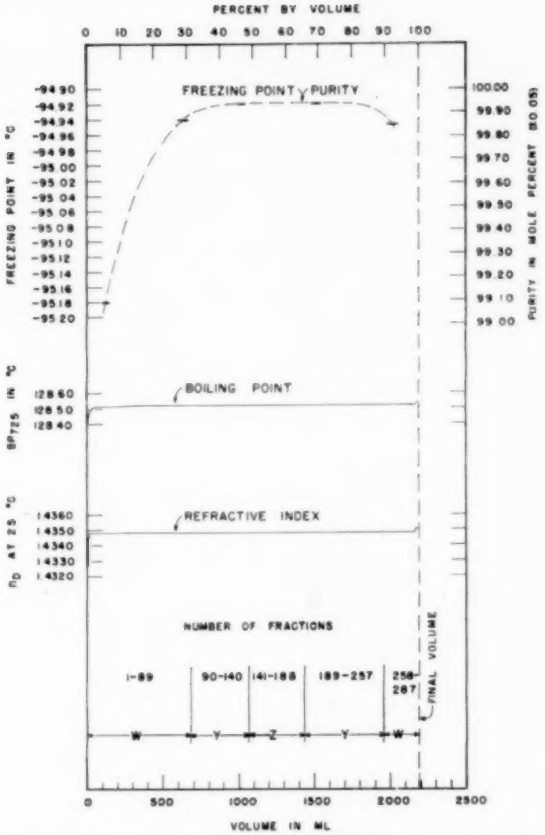

FIGURE 14.—*Results of the third distillation of n-propylcyclohexane.*

Azeotropic distillation with ethylene glycol monoethyl ether at 725 mm Hg in still 9 (3/13/46 to 5/3/46). See footnote "e" of table 2.

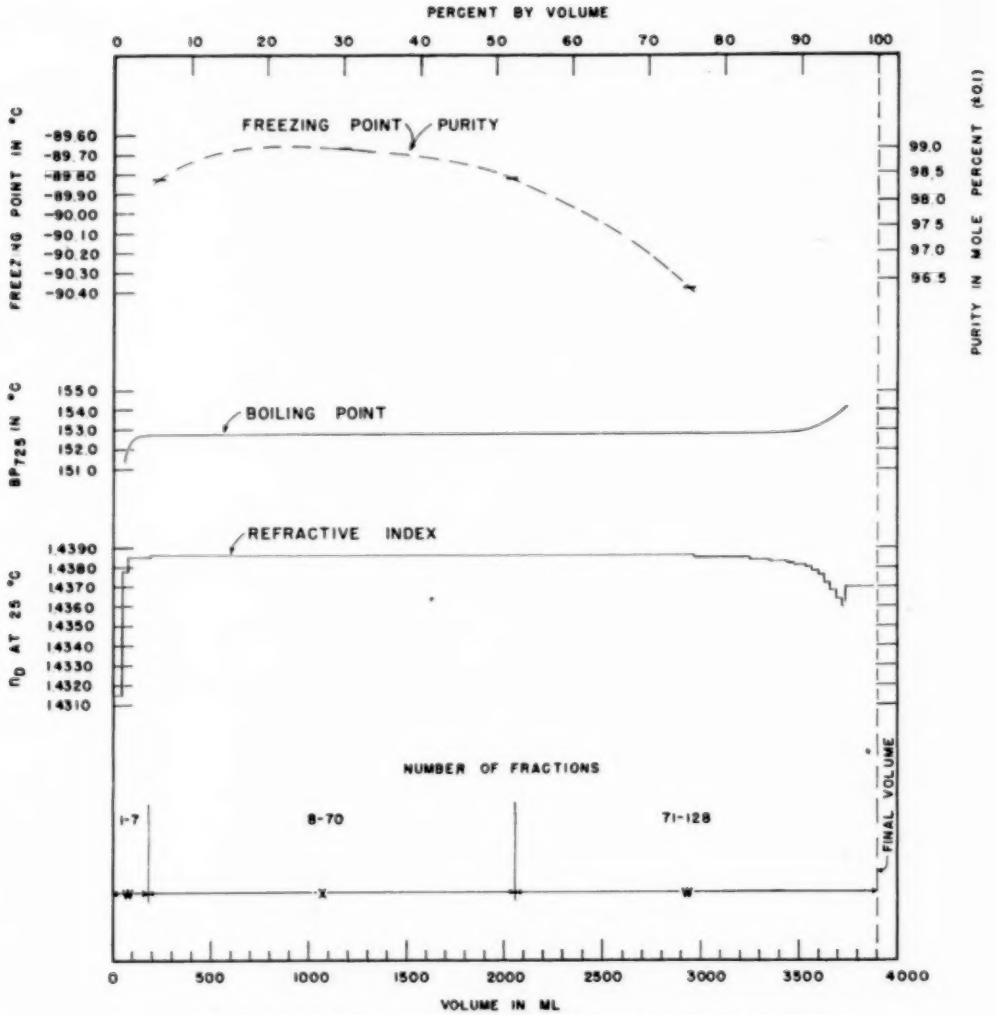

FIGURE 15.—*Results of the first distillation of isopropylcyclohexane.*

Regular distillation at 725 mm Hg in still 8 (10/18/45 to 11/12/45).

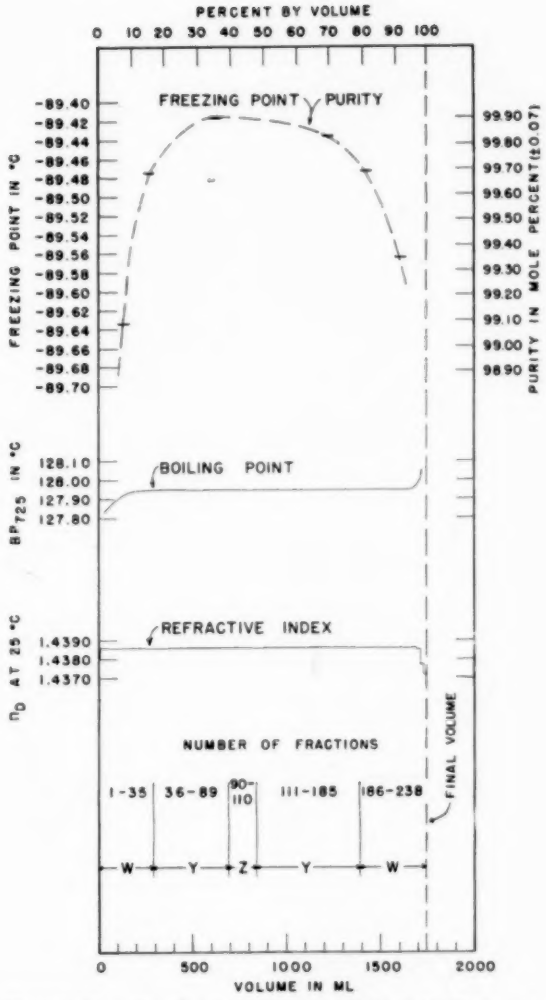

FIGURE 16.—*Results of the second and final distillation of isopropylcyclohexane.*

Azeotropic distillation with ethylene glycol monoethyl ether at 725 mm Hg in still 10 (3/2/46 to 4/12/46).

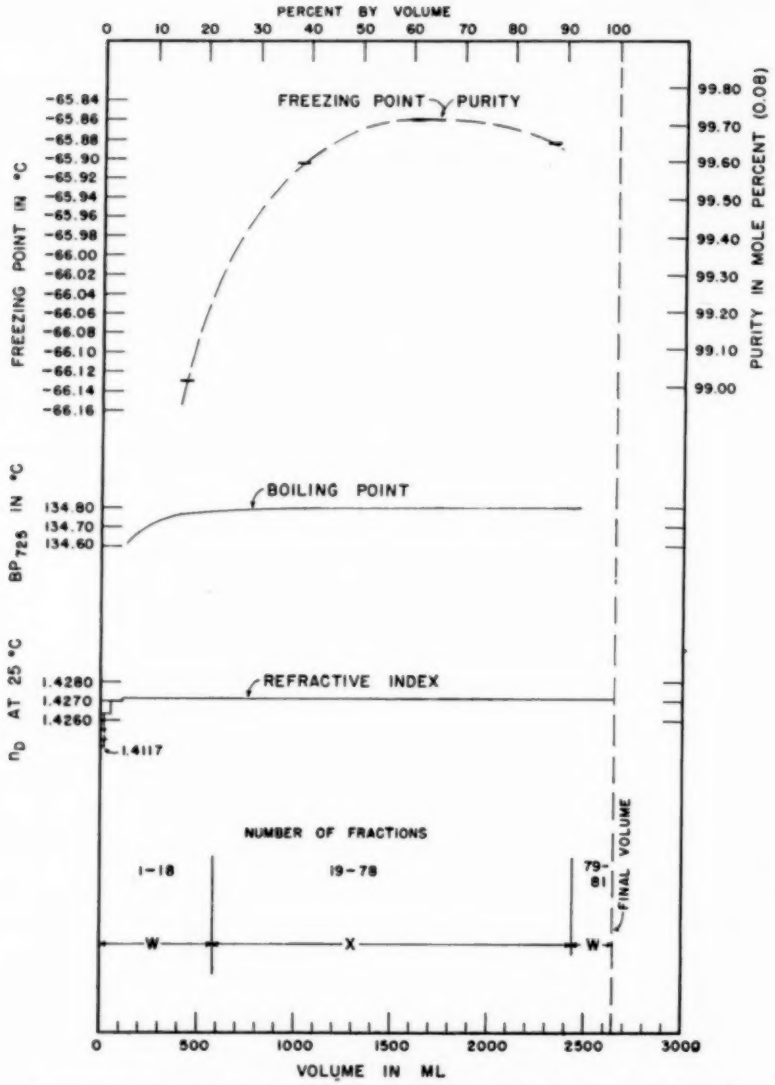

FIGURE 17.—*Results of the first distillation of 1,1,3-trimethylcyclohexane.*

Regular distillation at 725 mm Hg in still 7 (10/25/45 to 11/9/45).

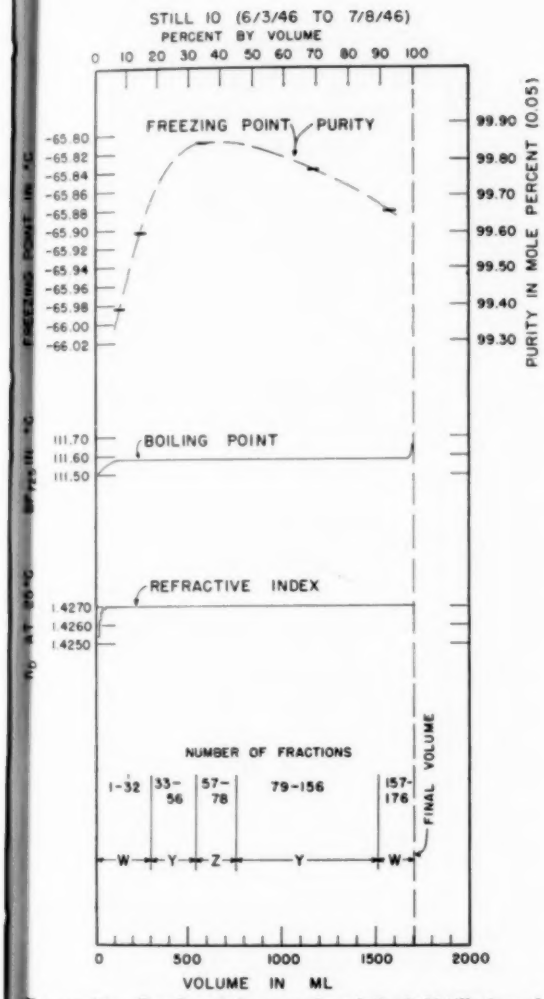

FIGURE 18.—*Results of the second and final distillation of 1,1,3-trimethylcyclohexane.*

Azeotropic distillation with ethylene glycol monomethyl ether at 725 mm Hg in still 10 (6/3/46 to 7/8/46).

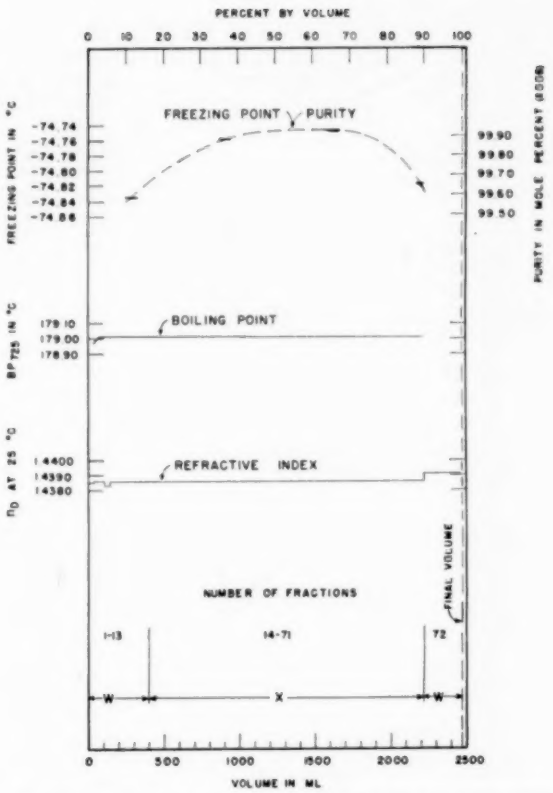

FIGURE 19.—*Results of the first distillation of n-butylcyclohexane.*

Regular distillation at 725 mm Hg in still 13 (5/15/45 to 5/31/45).

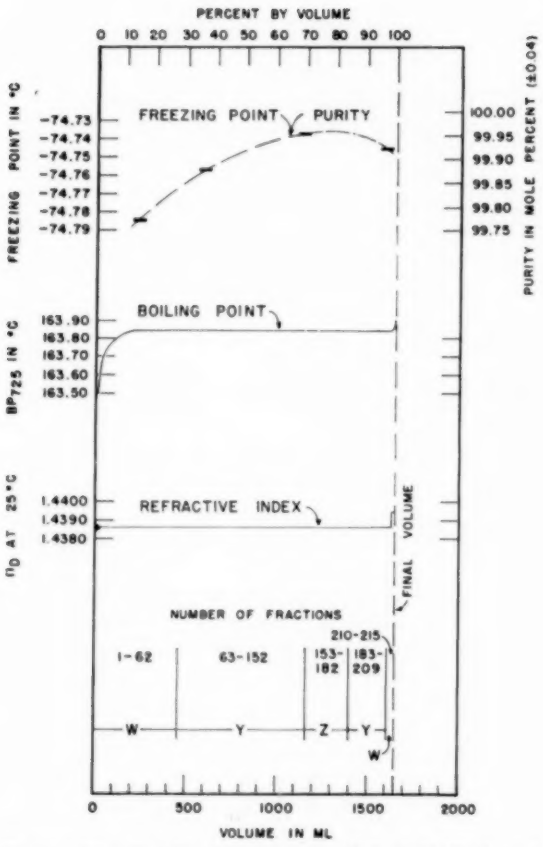

FIGURE 20.—*Results of the second and final distillation of n-butylcyclohexane.*

Azeotropic distillation with ethylene glycol monobutyl ether at 725 mm Hg in still 10 (7/23/46 to 8/31/46).

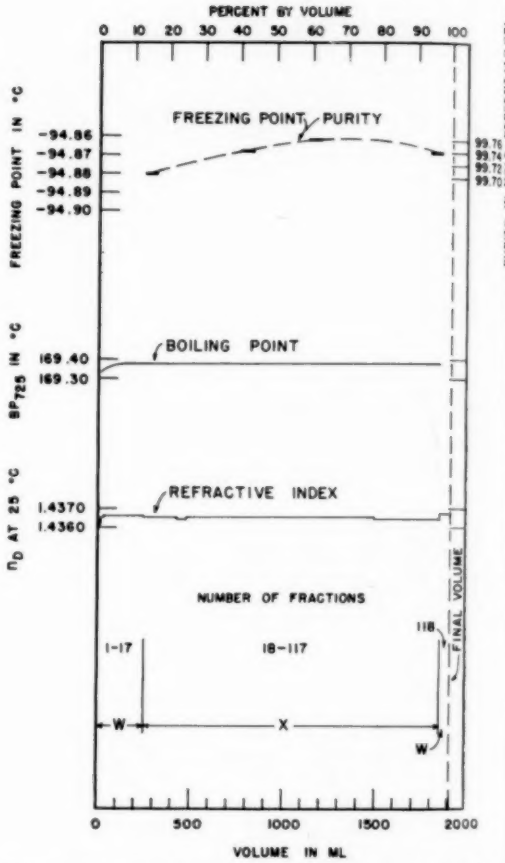

FIGURE 21.—*Results of the first distillation of isobutylcyclohexane.*

Regular distillation at 725 mm Hg in still 2 (12/7/45 to 1/21/46).

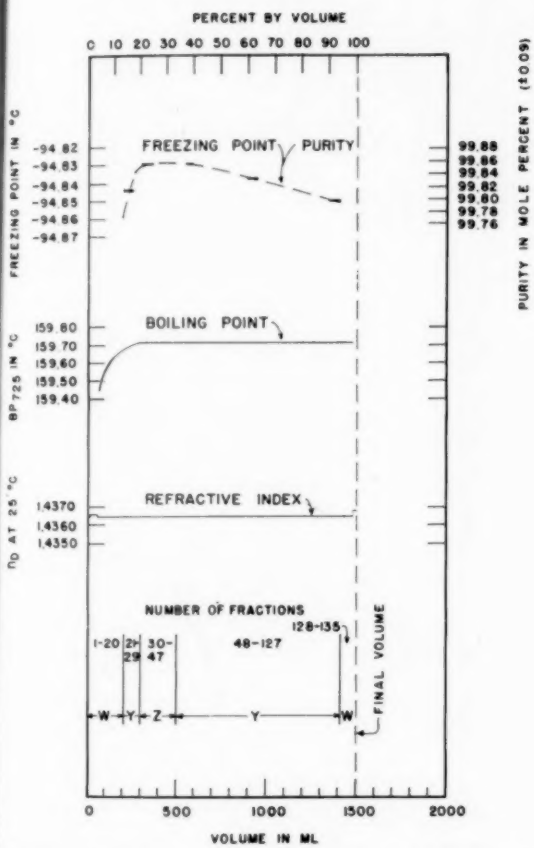

FIGURE 22.—*Results of the second and final distillation of isobutylcyclohexane.*

Azeotropic distillation with ethylene glycol monobutyl ether at 725 mm Hg in still 11A (7/25/46 to 8/20/46).

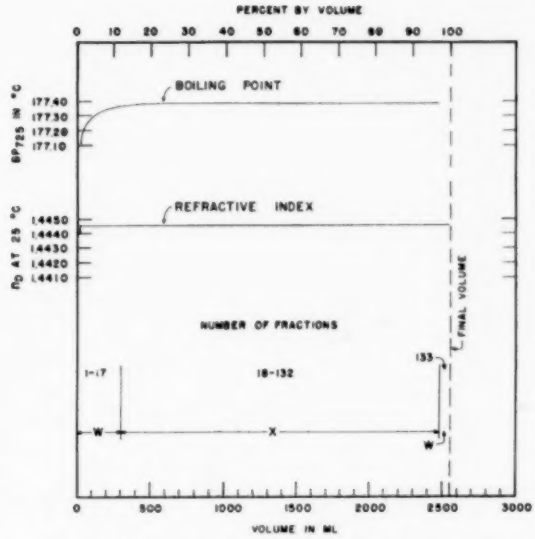

FIGURE 23.—*Results of the first distillation of sec-butylcyclohexane.*

Regular distillation at 725 mm Hg in still 12 (6/3/46 to 6/27/46).

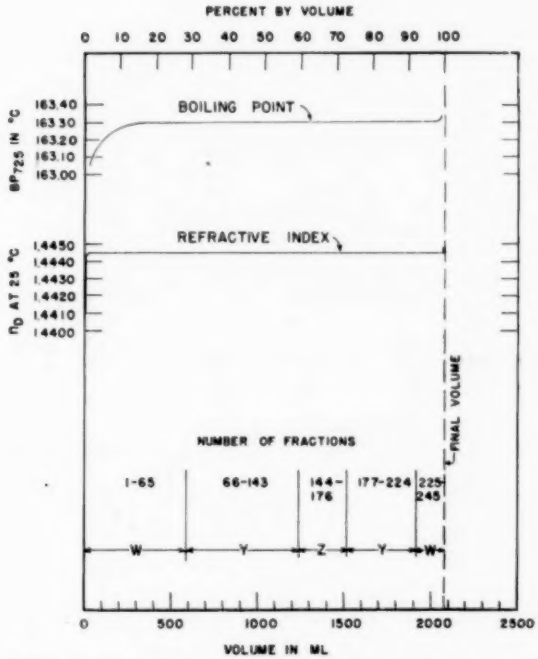

FIGURE 24.—*Results of the second and final distillation of sec-butylcyclohexane.*

Azeotropic distillation with ethylene glycol monobutyl ether at 725 mm Hg in still 11A (8/21/46 to 10/4/46).

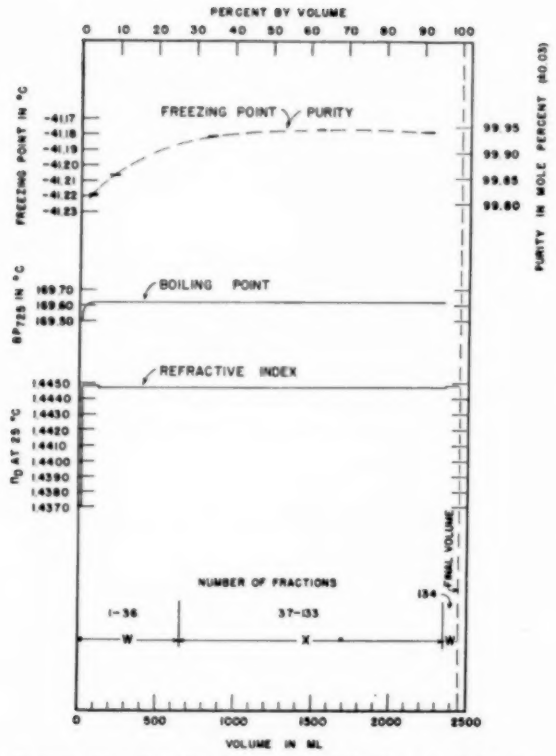

FIGURE 25.—*Results of the first distillation of tert-butylcyclohexane.*

Regular distillation at 725 mm Hg in still 12 (1/2/46 to 1/29/46).

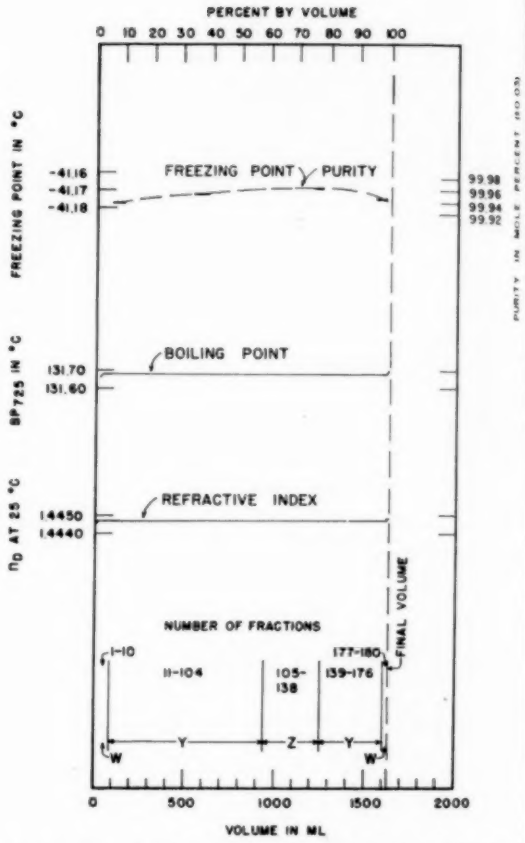

FIGURE 26.—*Results of the second and final distillation of tert-butylcyclohexane.*

Azeotropic distillation with ethylene glycol monoethyl ether at 725 mm Hg in still 8 (3/15/46 to 4/18/46).

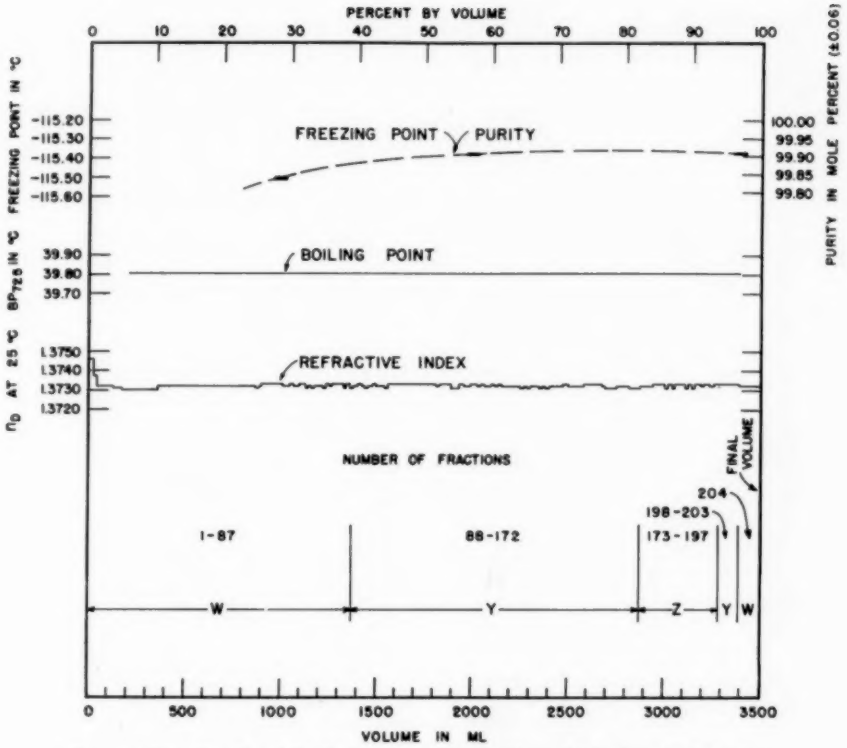

FIGURE 27.—*Results of the first and only distillation of 3,3-dimethyl-1-butene.*

Regular distillation at 725 mm Hg in still 9 (12/27/44 to 2/15/45).

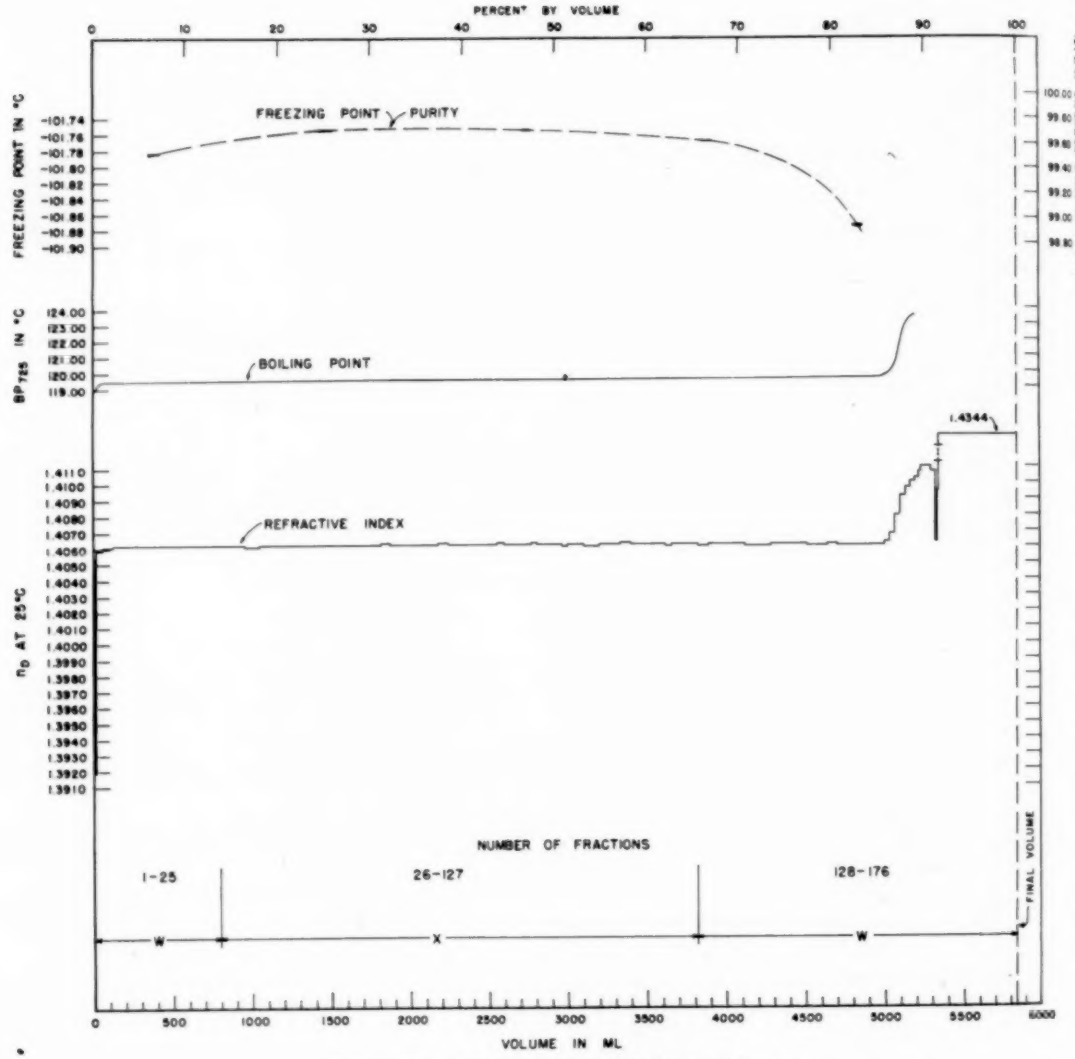

FIGURE 28.—*Results of the first distillation of 1-octene.*

Regular distillation at 725 mm Hg in still 13 (1/3/46 to 2/4/46). This is one of two distillations of similar material.

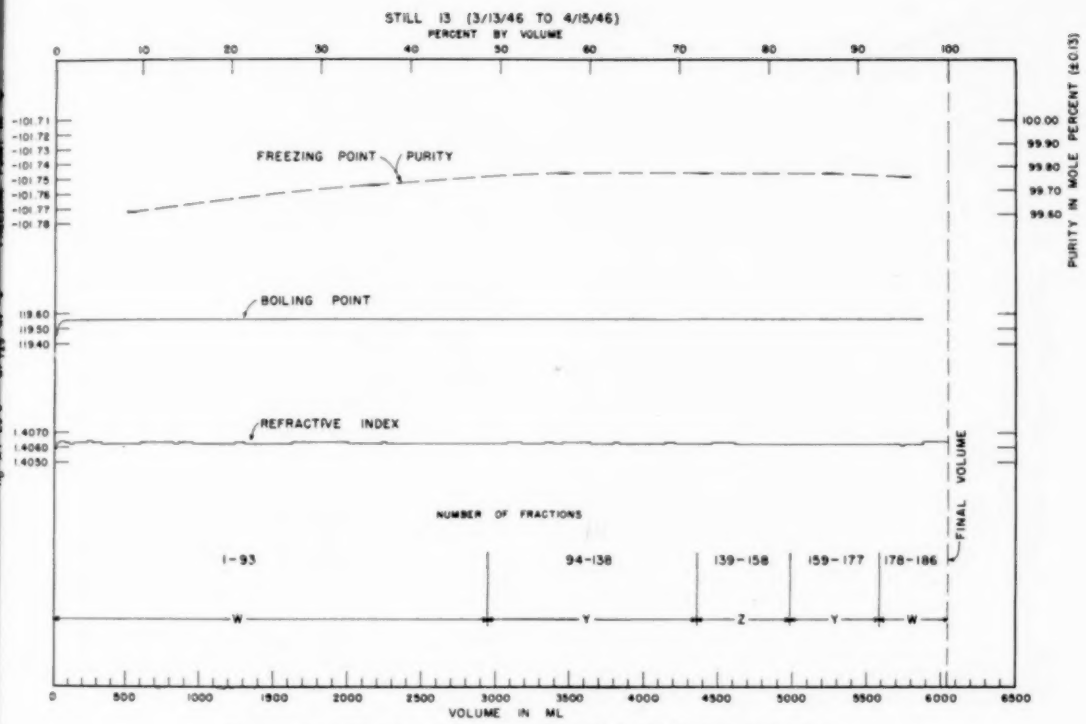

FIGURE 29.—*Results of the second and final distillation of 1-octene.*

Regular distillation at 725 mm Hg in still 13 (3/13/46 to 4/15/46).

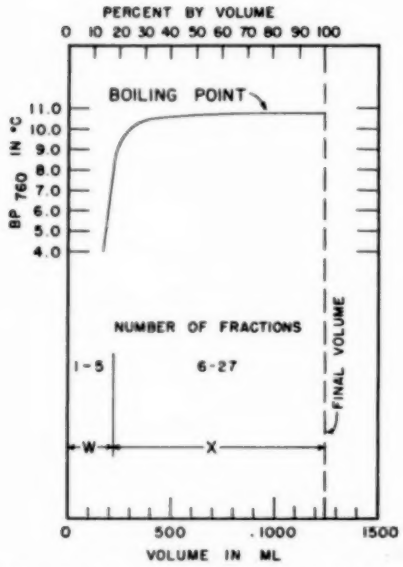

FIGURE 30.—*Results of the first distillation of 1,2-butadiene.*

Regular distillation at atmospheric pressure in still 1 (6/21/45 to 7/24/45).

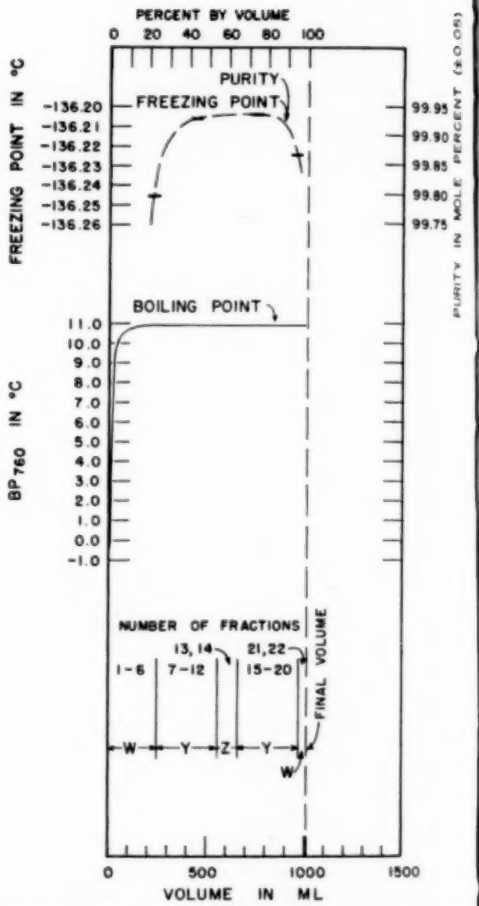

FIGURE 31.—*Results of the second and final distillation of 1,2-butadiene.*

Regular distillation at atmospheric pressure in still 1 (2/28/46 to 3/27/46).

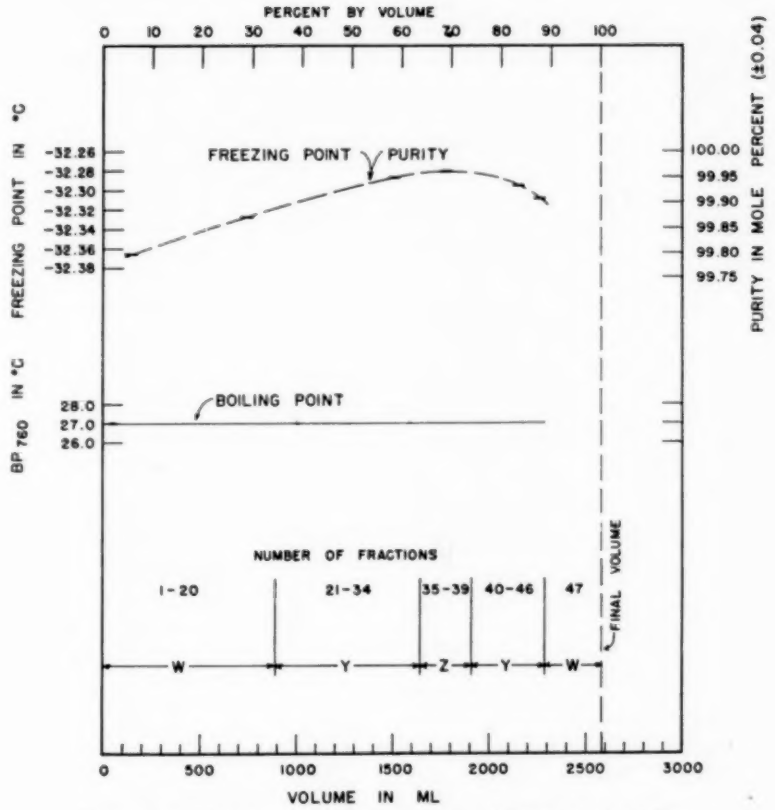

FIGURE 32.—*Results of the first and only distillation of 2-butyne.*

Regular distillation at atmospheric pressure in still 1 (11/8/45 to 1/7/46).

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Electrodeposition of Tungsten Alloys Containing Iron, Nickel, and Cobalt

By Abner Brenner, Polly Burkhead, and Emma Seegmiller

Methods of electrodepositing tungsten alloys with metals of the iron group have been developed. Some of the properties of the alloys have been determined and indicate that the alloys may be of commercial value. The plating solutions consist essentially of the appropriate metal salts, together with salts of certain hydroxy-organic acids in ammoniacal solutions at a pH of about 8.5. The deposits are smooth, strong, and brittle. The nickel and cobalt alloys become ductile on heating. As plated, the nickel and cobalt alloys have a hardness of 350 to 700 Vickers, and the iron alloy, 700 to 900 Vickers. The alloys undergo precipitation hardening and the cobalt-tungsten alloys retain their hardness when hot.

I. Introduction

This report covers methods of codepositing tungsten with iron, nickel, or cobalt and the study of the properties and applications of these alloys. A comprehensive research was conducted by a number of persons over a period of several years, during which hundreds of plating baths and deposits were prepared and studied. Although this investigation is not complete, it is advisable to publish the results thus far obtained in order to permit others to determine the commercial applicability of the alloys, and to conduct further studies.

Methods have been worked out for electrodepositing alloys of tungsten with iron, cobalt, or nickel. Some of the measured properties indicate that these alloys may be suitable for certain engineering applications. The plating solutions consist essentially of the appropriate metal salts, together with salts of certain hydroxy-organic acids in ammoniacal solutions at a pH of about 8.5. Deposits as thick as several hundredths of an inch can be made with good current efficiency. They are smooth, strong, and hard, and some show precipitation hardening.

II. Experiments With Published Baths

1. Deposition of Alloys From Acid Solutions

When this investigation was started, most of the published work on depositions of tungsten alloys dealt with acid baths. Between 1935 and 1940, interest was aroused in this subject, especially the nickel-tungsten alloys. Harry H. Armstrong and Arthur B. Menefee [1 to 8][1] patented a process and organized the Tungsten Electrodeposit Corporation. Their patents emphasized the use of fluorides in acid baths. M. L. Holt and his coworkers [17, 18, 19] published papers on the electrodeposition of tungsten with nickel, iron, and cobalt.

When the work of these investigators was repeated, deposits were obtained that contained the reported proportions of tungsten, but they had inferior physical properties, being weak and brittle, and appeared to contain oxide. Deposits more than a thousandth of an inch thick were rough, and the cathode current efficiencies were low.

In addition to trying the solutions of published composition experiments were made with acid baths containing the tungsten as complex ions, such as borotungstates, phosphotungstates, or fluotungstates. The deposits obtained from these solutions were not superior to those obtained from the simple Holt bath. The only advantage of the complex formation was that it permitted larger concentrations of tungsten to be held in solution (as compared with the few grams permissible in the Holt bath) so that the control of the composition of the bath was not critical.

In all the acid baths "tungsten blue," containing

[1] Figures in brackets indicate the literature references at the end of this paper.

compounds of tungsten with a valence lower than 6, formed at the cathode, and eventually the whole solution became colored. It is thought that the inclusion of partially reduced tungsten compounds might be the cause of the oxide content of the deposits and their poor physical characteristics. Attempts were made to keep the bath free of tungsten blue by bubbling air around the cathode, or by the judicious additions of hydrogen peroxide, but the deposits were not improved.

2. Deposition of Alloys From Acid Solutions

Because of the lack of success with acid plating solutions, attention was directed to the alkaline baths. Holt showed that the deposit that C. G. Fink had obtained from the electrolysis of an alkaline tungstate solution was not pure tungsten, but an alloy containing iron [13, 15], and that alloys of tungsten with other metals could be obtained from carbonate solutions [16, 20]. These solutions, however, yielded only a small quantity of deposit before they ceased to plate and hence were not suitable for commercial application. Several Russian workers obtained nickel-tungsten alloys [9, 14, 22] from ammoniacal solutions. When their work was repeated, this process was found to be more practicable than Holt's. A paper by Vaaler and Holt [25] on the electrodeposition of nickel-tungsten alloys from ammoniacal citrate solutions appeared while this report was in preparation. As the process described in their paper is similar to the one developed here, it will be discussed in more detail under the deposition on nickel-tungsten alloys.

III. Experimental Methods

No special plating technics were used in this investigation. The plating baths varied in size from small beakers for the initial trials to 6-liter Pyrex cylinders for baths used in the plating of specimens for the study of properties. The largest bath contained about 15 liters. External heating along with thermoregulators controlled the temperature to about ± 3 deg C, and the solution was kept at a constant level by a float valve.

In the initial experiments, which were made on a beaker scale, for determining the composition of deposits as a function of the bath composition and plating conditions, a cylindrical gold rod about 5 mm in diameter was used as cathode. The current density on a rod is more uniform than on a flat sheet. The color of the gold made it easy to observe whether plating had occurred. The alloy deposits could readily be dissolved from the gold without attacking the latter, by pouring a mixture of nitric and hydrofluoric acids over the gold rod placed in a platinum test tube.

Thick deposits were required for the measurement of physical properties. These deposits were made on copper tubing that had an outside diameter of 5 mm and a wall thickness of 0.25 mm. The end of the tube was closed with a plug to prevent contamination of the solution with copper, and a length of from 15 to 30 cm was plated in a 6-liter Pyrex cylinder. Separation of the deposit from the copper was effected by removing the latter chemically by the action of sodium polysulfide (approximately M Na_2S_2), followed by immersion in a solution of sodium cyanide (about 100 g/liter), which served to loosen and dissolve the copper sulfide formed by the polysulfide treatment. The treatments with the polysulfide and cyanide were alternated at intervals of from 15 minutes to 1 hour.

This procedure for stripping the copper away from the alloy deposit constituted the first test of soundness of the alloy. Sound deposits came through the stripping operation intact, whereas others, particulary those that had been deposited at high current densities or from certain unsatisfactory baths, crumbled.

IV. Electrodeposition of Alloys

1. General Considerations

The results of the investigation on deposition are discussed in three sections: alloys of cobalt-tungsten; nickel-tungsten; and iron tungsten. Although the methods of plating are similar, the differences are sufficiently great, especially in the case of the iron alloys, to require separate descriptions. The physical properties of all three alloys will be discussed in connection with each property. The investigation of the cobalt-tungsten alloys has been the most thorough, and that of the iron alloys the least. The work with the latter was made more difficult by the two states of oxidation of iron, and much work needs to be done on these alloys. From our experience, a successful plating solution for codepositing tungsten with a metal of the iron group requires, in

addition to compounds containing the two metals, a salt of certain hydroxy-organic acids, ammonium compounds, and an excess of NH_4OH to bring the pH to 8.0 or above. Of the hydroxy acids investigated, those aliphatic hydroxy-carboxylic acids in which the sum of the hydroxy and carboxyl groups is greater than three operate the best. One exception to this rule is hydroxy-acetic acid, which contains only one hydroxyl and one carboxyl group, but yields fairly satisfactory baths. A practical requirement is that the salts of the acid be quite soluble, otherwise a bath of satisfactory metal content cannot be obtained. Among the satisfactory acids may be mentioned tartaric, malic, gluconic, saccharic, citric and hydroxyacetic. On the other hand, salts of organic acids such as lactic, acetic, oxalic, and salicylic, and of inorganic acids, were not satisfactory. Mucic acid was of limited value because of the low solubility of its salts. Some of the amino-acids were almost usable. Glutamic acid and glycine yielded fairly satisfactory deposits, which, however, were not quite equal in soundness to those from the hydroxy acids. Of the hydroxy acids commercially available, hydroxyacetic acid is one of the cheapest, costing only about one-fifth as much as tartaric acid.

It is not possible to make general statements regarding the concentrations of each constituent of the bath, because the solubility of one substance is affected by the presence of the other constituents. Deposits have been obtained from solutions that range in composition from 100 g/liter of the iron group metal and 25 g/liter of tungsten, to 10 g/liter of the iron group metal and 150 g/liter of tungsten. The salts of the organic acids have been used in concentrations as high as 600 g/liter and the ammonium salts as high as 300 g/liter.

Most of the plating was done above 90° C and at a pH above 8.5. The cathode current density varied from 1 to 30 amp/dm².

2. Electrodeposition of Cobalt-Tungsten Alloys

Introduction.—The main commercial interest in the cobalt-tungsten alloys stems from their hardness [23]. They are related to stellite, an alloy of cobalt and chromium with tungsten or molybdenum, except that they contain no chromium. Attempts made in this investigation to electrodeposit a ternary alloy containing an appreciable amount of chromium have not been successful. The hot-hardness of alloys such as stellite makes them useful for high-speed tools and for engineering applications where good strength or hardness at elevated temperatures is required. At temperatures below 700° C, high-speed tool-steels may have a greater hardness than stellite, but at higher temperatures, the hardness of tool-steel rapidly decreases, and the stellite is superior. As will be shown in the discussion of properties, the cobalt-tungsten alloys have a hot-hardness approaching that of stellite.

Planting Solutions. Preparation and Solubility Relations.—The plating solution that was considered most satisfactory for the electrodeposition of cobalt-tungsten alloys had the following composition:

	g/liter
Cobalt (as chloride or sulfate)	25
Tungsten (as sodium tungstate)	25
Rochelle salt	400
Ammonium chloride or sulfate	50
Ammonium hydroxide to a pH of 8.5	

The operating conditions were temperature, 90° C or above; pH, 8.5 or above; current density, 2 to 5 amp/dm². Although the concentrations given are preferable, they are not in any way critical. The concentration of tungsten may vary from zero to saturation, depending on the composition of deposit desired. In the absence of tungsten, the bath gives a cobalt deposit that is rather dark in color, and for depositing cobalt, this bath has no advantage over an ordinary cobalt bath of low pH. As tungsten is added, the deposits become brighter. The concentration of the cobalt in the bath may vary from 0.5 g/liter to saturation, and that of Rochelle salt over wide limits. If either the ammonium salt or the Rochelle salt is entirely omitted, the behavior of the bath is considerably different, as will be discussed later.

There is an advantage in employing plating solutions that are high in metal content, because higher current densities can be used and thicker smooth deposits can be obtained. For this reason most attention was given to concentrated baths. Solutions saturated with salts, however, are not satisfactory, because the deposits are more likely to be pitted.

It was found that when strong solutions of the above types were kept at the temperature of operation (usually 90° to 100° C), precipitates formed and the bath composition was altered. To avoid

the study of unstable baths, solutions of varying composition were sealed in bottles and allowed to stand on a steam bath for about a week, so that they would come to chemical equilibrium, and were then analyzed. In this way some solutions that initially seemed capable of holding in solution high concentrations of metals were found to be unstable. Although the principle of the solubility product is not strictly applicable to these strong solutions, it was found that the product of the concentrations of cobalt and of tungsten (in g/liter) was fairly constant, when the concentrations of the other constituents were fixed. This relation made it possible to indicate the approximate maximum concentrations of cobalt and tungsten that could be used in a given solution. Some data illustrating the application of the solubility principle are given in table 1, part A.

TABLE 1.—*Solubility relations of cobalt and tungsten in ammoniacal solutions of* pH *8.5*

A. Application of the solubility product principle (each solution contained ammonium chloride, 50 g/liter)

No.	Salt of organic acid			Metal concentration								
	Type	Concentration		Initial				Final				Solubility product, Co×W (g/liter)²
				Co		W		Co		W		
		Molarity	g/liter	Molarity	g/liter	Molarity	g/liter	Molarity	g/liter	Molarity	g/liter	
1	Sodium hydroxyacetate	2.6	260	0.85	50	0.13	25	0.64	38	0.02	4	
2	do	2.6	260	.85	50	.27	50	.47	28	.03	6	
3	do	2.6	260	.85	50	.54	100	.14	8	.11	20	
4	Ammonium hydroxyacetate	2.6	245	.85	50	.13	25	.78	46	.04	8	
5	do	2.6	245	.85	50	.27	50	.54	32	.08	14	
6	do	2.6	245	.85	50	.54	100	.25	15	.12	22	
7	Potassium malate	2.2	470	.85	50	.27	50	.54	32	.18	33	
8	do	2.2	470	.85	50	.54	100	.40	23	.28	52	
9	Rochelle salt	1.4	400	.85	50	.27	50	1.0	58	.29	53	
10	do	1.4	400	.42	25	.54	100	0.54	32	.40	72	

B. Effect of concentrations of salts of organic acids and of ammonium salts on the solubility product

	Salt			NH_4Cl		Solubility product, Co×W (g/liter)²
	Type	Concentration		Molarity	g/liter	
		Molarity	g/liter			
11	Rochelle salt	1.4	400	1.0	50	
12	do	2.1	600	1.0	50	
13	do	.7	200	1.0	50	
14	Ammonium tartrate	1.3	245	1.0	50	
15	Sodium hydroxyacetate	2.6	260	1.0	50	
16	do	2.6	260	4.0	200	
17	do	5.2	520			
18	do	5.2	520	1.0	50	
19	Ammonium hydroxyacetate	2.6	245	1.0	50	
20	do	2.6	245	4.0	200	
21	do	5.2	490	1.0	50	
22	Potassium malate	2.2	470	1.0	50	
23	Ammonium malate	2.2	376	1.0	50	
24	Ammonium sulfate	2.3	300			
25	Ammonium sulfamate	2.0	250			(1)
26	Ammonium fluoborate	1.9	200			(1)
27	Ammonium bifluoride	3.5	200			(1)
28	Sodium hexametaphosphate	.3	200			(1)
29	Ammonium acid phosphite	1.2	120			(1)

[1] Less than 75.

TABLE 2.—*Composition of cobalt-tungsten alloys*

(In addition to the constituents listed below, each solution contained ammonium chloride, 50 g/liter, unless otherwise stated, and was operated at 90° C and a pH of 8.5.)

No.	W/Co (weight)	Bath composition							Cathode efficiency—		Tungsten in deposit—	
		Co		W		Organic salt			2 amp/dm²	5 amp/dm²	2 amp/dm²	5 amp/dm²
		Molarity	g/liter	Molarity	g/liter	Type	Concentration					
							Molarity	g/liter				
TARTRATE												
									Percent	*Percent*	*Percent*	*Percent*
1	0.12	0.68	40	0.03	5	Na, K	1.40	400	100	100	8	12
2	.20	.42	25	.03	5	Na, K	1.40	400	97	.....	10	18
3	.30	.85	50	.08	15	Na, K	1.40	400	.....	.....	12	24
4	.30	.85	50	.08	15	Na, K	1.40	400	100	100	13	20
5	.50	.68	40	.12	20	Na, K	1.40	400	.....	.....	14	20
6	.50	.27	16	.04	8	Na, K	0.70	200	100	.....	15	.....
7	.67	.10	6	.02	4	Na, K	.35	100	95	.....	18	.....
8	.67	.25	15	.05	10	Na, K	.35	100	100	100	20	31
9	.70	.85	50	.20	35	Na, K	1.40	400	97	95	13	24
10	.70	.85	50	.20	35	Na, K	1.40	400	97	99	20	24
11	.75	.68	40	.16	30	Na, K	1.40	400	.....	.....	21	26
12	1.0	.42	25	.14	25	Na, K	1.40	400	93	.....	20	27
13	1.0	.42	25	.14	25	Na, K	0.70	200	97	91	20	27
14	1.0	.25	15	.08	15	Na, K	.70	200	92	97	15	28
15	1.0	.25	15	.08	15	Na, K	.35	100	100	.....	14	22
16	1.0	.20	11	.05	11	Na, K	.35	100	90	93	18	29
17	1.0	.20	12	.06	13	Na, K	.35	100	95	97	22	28
18	1.3	.10	6	.04	8	Na, K	.35	100	97	.....	18	.....
19	1.3	.20	12	.08	16	Na, K	.35	100	92	97	8	29
20	1.5	.20	12	.09	18	Na, K	.70	200	92	100	16	28
21	3.0	.10	6	.09	17	Na, K	.35	100	92	.....	32	.....
22	3.3	.10	6	.10	20	Na, K	.35	100	90	98	31	33
23	3.5	.25	15	.30	53	Na, K	.88	250	94	95	29	34
24	4.4	.20	12	.30	55	Na, K	.88	250	90	91	35	38
25	6.0	.10	6	.20	35	Na, K	.35	100	100	98	35	41
CITRATE												
26	0.14	0.60	35	0.03	5	Na	0.60	200	87	70	23	27
27	.14	.60	35	.03	5	NH_4	1.20	300	83	78	23	22
28	.14	.60	35	.03	5	NH_4	1.20	300	70	77	23	24
29	.50	.42	25	.07	13	Na	0.60	200	66	59	30	42
30	1.0	.42	25	.14	25	Na	.60	200	78	71	41	39
31	6.0	.10	6	.20	35	Na	.60	200	[a] 26	.....	[a] 42	.....
32	6.0	.20	12	.38	70	Na	.60	200	[a] 27	.....	[a] 42	.....
33	12.0	.10	6	.38	70	Na	.30	100	[a] 26	.....	[a] 50	.....
34	35.0	.02	1	.20	35	Na	.30	100	[a] 31	.....	[a] 57	.....
MALATE												
35	0.50	0.85	50	0.14	25	K	1.5	310	89	85	11	12
36	.67	.25	15	.06	10	NH_4	0.7	125	91	95	17	27
37	1.0	.85	50	26	50	K	1.5	310	68	76	10	15
38	2.0	.85	50	.54	100	NH_4	1.5	270	85	93	24	27
39	4.0	.42	25	.54	100	K	1.5	310	100	100	24	26

See footnotes at end of table.

TABLE 2.—*Composition of cobalt-tungsten alloys*—Continued

No.	W/Co (weight)	Bath composition							Cathode efficiency—		Tungsten in deposit—	
		Co		W		Organic salt						
		Molarity	g/liter	Molarity	g/liter	Type	Concentration		2 amp/dm²	5 amp/dm²	2 amp/dm²	5 amp/dm²
							Molarity	g/liter				
HYDROXYACETATE												
40	0.15	1.7	100	0.08	15	Na	5.0	500	.....	.....	.....	
41	.25	1.7	100	.14	25	NH_4	5.0	500	.....	.....	8	
42	.30	0.85	50	.08	15	Na	5.0	500	.....	.....	6	
43	2.0	.42	25	.28	50	NH_4	5.0	500	97	96	21	
GLUCONATE												
44	0.90	0.34	20	0.10	17	NH_4	0.50	100	[a] 90	94	[a] 5	
45	.90	.68	40	.20	35	NH_4	.50	100	[a] 93	95	[a] 3	
46	1.8	.34	20	.20	35	NH_4	.50	100	[a] 98	98	[a] 8	
47	1.8	.68	40	.40	70	NH_4	.50	100	.....	94	.....	
48	6.0	.10	6	.20	35	NH_4	.50	100	[b] 97	95	[b] 33	
GLUTAMATE												
49	0.30	0.85	50	0.08	15	Na, K	1.35	280	.....	.....	.....	
LACTATE												
50	3.0	0.08	5	0.08	15	K	4.5	570	90	.....	19	
ACETATE												
51	1.0	0.20	12	0.08	15	Na	3.0	400	.....	87	.....	
INORGANIC												
52 [f]	0.5	0.39	23	0.07	12	.....	.....	.....	60	52	20	

[a] Bath contains NH_4Cl, 200 g/liter.
[b] Bath contains NH_4Cl, 100 g/liter.
[c] Bath contains no NH_4Cl.
[d] Bath contains NH_4Cl, 300 g/liter.
[e] Bath contains NH_4Cl, 150 g/liter.
[f] Bath contains $(NH_4)_2SO_4$, 200 g/liter.
[g] 3 amp/dm².
[h] 3½ amp/dm².
[i] Bath contains $(NH_4)_2SO_4$, 300 g/liter.

The manner in which the solubility of cobalt and tungsten are affected by the concentrations of the other constituents of the solution is shown in table 1, part B. The values of the solubility product given here are rough guides to the variations in solubility of the metals with a change in composition of the plating solutions. In applying the solubility product principle to the preparation of a given solution, the maximum solubility of the individual metals must not be exceeded. For practical purposes, the upper limit of cobalt is about 50 g/liter (although concentrations of 10 g/liter have been attained), and the upper limit of tungsten is about 150 g/liter (although a concentration of 200 g/liter has been attained).

The data in table 1, part B, show that a high concentration of the organic acid permits high concentrations of cobalt and tungsten, which are much less soluble in the absence of the organic salts. The tartrate solution has the best solubility for cobalt and tungsten. The use of ammonium salts of organic acids instead of sodium salts

wers the solubility product in the tartrate solution, increases it considerably in the hydroxyetate solution, and has little effect in the malate lution.

The solubility of tungstates in ammoniacal lutions in the absence of cobalt is interesting. n an ammoniacal solution containing no ammonm salts, sodium tungstate ($Na_2WO_4.2H_2O$) will ssolve to the extent of 600 g/liter (equivalent to 00 g of tungsten). If a strong solution of sodium ngstate is added to a strong solution of ammonm sulfate, a precipitate forms that will not dissolve entirely on heating. However, if the dium tungstate solution is made ammoniacal efore it is added to the ammonium salt solution, stable solution results, which can hold 200 g of dium tungstate per liter in the presence of 300 g ammonium sulfate per liter. The salts of the ydroxy acids do not seem to affect appreciably e solubility of tungstates. A solution similar the plating solutions, for example, containing 400 g of Rochelle salt per liter and 100 g of ammonium sulfate per liter will dissolve 400 g of sodium tungstate per liter.

Factors affecting the composition of deposits.—Deposits containing up to 50 percent of tungsten have been obtained, but the deposits that are sound enough for engineering applications do not contain over 35 percent of tungsten. The most influential factors on the composition of the deposit were: the metal ratio in the solution (W/Co); the type of organic hydroxy acid used; and the current density. Other variables, such as the concentration of the solution, pH, and temperature, had only a minor effect on the composition of the deposit; but in some cases had a large effect on its physical properties.

The effects of variations in composition of the plating solution on the composition of the deposit are illustrated in table 2, the effects of current density in table 3, and the effects of temperature in table 4.

TABLE 3.—*Effect of current density on composition of cobalt-tungsten alloys*

(Each solution contained ammonium chloride, 50 g/liter. Temperature, 90° C, pH 8.5.)

No.	Bath composition								Current Density	Cathode efficiency	Tungsten in deposit
	W/Co (weight)	Co		W		Organic salt					
		Molarity	g/liter	Molarity	g/liter	Type	Concentration				
							Molarity	g/liter			
					TARTRATE						
									amp/dm²	*Percent*	*Percent*
	0.13	0.68	40	0.03	5	Na,K	1.4	400	1	100	4
	.13	.68	40	.03	5	Na,K	1.4	400	2	100	8
	.13	.68	40	.03	5	Na,K	1.4	400	3	100	10
	.13	.68	40	.03	5	Na,K	1.4	400	5	100	12
	.30	.85	50	.09	15	Na,K	1.4	400	1	100	9
	.30	.85	50	.09	15	Na,K	1.4	400	2	.....	12
	.30	.85	50	.09	15	Na,K	1.4	400	3	.....	16
	.30	.85	50	.09	15	Na,K	1.4	400	5	.....	19
	.30	.85	50	.09	15	Na,K	1.4	400	10	.....	26
	1.0	.42	25	.13	25	Na,K	0.70	200	1	88	9
	1.0	.42	25	.13	25	Na,K	.70	200	2	87	21
	1.0	.42	25	.13	25	Na,K	.70	200	5	91	25
	1.0	.42	25	.13	25	Na,K	.70	200	10	82	31
	1.0	.25	15	.09	15	Na,K	.35	100	1	100	14
	1.0	.25	15	.09	15	Na,K	.35	100	2	100	18
	1.0	.25	15	.09	15	Na,K	.35	100	5	100	24
	6.0	.08	6	.20	35	Na,K	.35	100	1	95	14
	6.0	.08	6	.20	35	Na,K	.35	100	2	.....	35
	6.0	.08	6	.20	35	Na,K	.35	100	3	98	33
	6.0	.08	6	.20	35	Na,K	.35	100	5	98	41

TABLE 3.—*Effect of current density on composition of cocalt-tungsten alloys*—Continued

(Each solution contained ammonium chloride, 50 g/liter. Temperature, 90° C, pH 8.5.)

No.	Bath composition								Current Density	Cathode efficiency	Tungsten in deposit
	W/Co (weight)	Co		W		Organic salt					
		Molarity	g/liter	Molarity	g/liter	Type	Concentration				
							Molarity	g/liter			
CITRATE											
21	0.14	0.60	35	0.03	5	NH_4	1.2	300	2	83	
22	.14	.60	35	.03	5	NH_4	1.2	300	3	.....	
23	.14	.60	35	.03	5	NH_4	1.2	300	5	78	
GLUCONATE											
24	1.0	0.34	20	0.12	20	NH_4	1.0	220	1	100	
25	1.0	.34	20	.12	20	NH_4	1.0	220	2	100	
26	1.0	.34	20	.12	20	NH_4	1.0	220	3	100	
27	1.0	.34	20	.12	20	NH_4	1.0	220	5	100	
28	1.8	.34	20	.20	35	NH_4	0.50	110	3	98	
29	1.8	.34	20	.20	35	NH_4	.50	110	5	98	
30	1.8	.34	20	.20	35	NH_4	.50	110	10	94	
31	6.0	.08	6	.20	35	NH_4	.50	110	1	95	
32	6.0	.08	6	.20	35	NH_4	.50	110	3.5	97	
33	6.0	.08	6	.20	35	NH_4	.50	110	5.0	95	
HYDROXYACETATE											
34	0.25	1.6	100	0.13	25	NH_4	5.0	500	2	.....	
35	.25	1.6	100	.13	25	NH_4	5.0	500	5	.....	
36	.25	1.6	100	.13	25	NH_4	5.0	500	10	.....	
37	.25	1.6	100	.13	25	NH_4	5.0	500	15	.....	

TABLE 4.—*Effects of bath temperature on composition of cobalt-tungsten alloys*

No.	Organic salt			Co		W		Current efficiency at—			Tungsten in deposit at—		
	Type	Concentration		Molarity	g/liter	Molarity	g/liter	25° C	55° C	90° C	25° C	55° C	90° C
		Molarity	g/liter										
								Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1	Na citrate	0.6	200	0.20	12	0.40	74	.....	[a] 12	27	.....	62	6
2	Rochelle salt	.4	160	.10	6	.20	35	50	82	96	26	36	4

[a] Bath operated at 45°C instead of 55°C.

The main conclusions derived from these data are as follows:

Metal-ratio.—The tungsten-cobalt ratio of the bath is the most important factor affecting the composition of the deposit. As this ratio increases, the percentage of tungsten in the deposit also increases, but the increase is slight when the solution contains more than three times as much tungsten as cobalt. (See figs. 1 and 3). The deposit does not contain more than about 50 per cent of tungsten, even if the tungsten-cobalt ratio in the solution is as high as 35.

The citrate solution with a low ratio of tungsten to cobalt (solution containing cobalt 35 g/liter and tungsten 5 g/liter, No. 21, table 3) deserves special consideration because the tungsten-cobalt ratio of the deposit (0.3) is higher than in the solution (0.14). This situation indicates that

tungsten has reversed its role and is the more readily deposited metal. At any rate, in the citrate solution, cobalt and tungsten must have deposition potentials that are close together, otherwise it would be difficult to explain why there is so little variation in the composition of the deposit with current density.

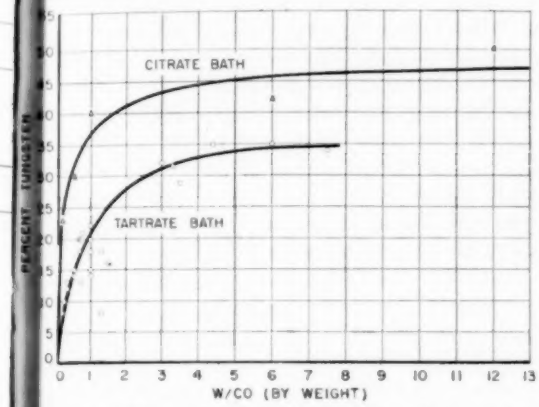

FIGURE 1.—*Effect of tungsten-cobalt ratio on the percentage of tungsten in the deposit from tartrate and citrate alloy baths of various compositions.*

The current density is 2 amp/dm².

Current density.—The content of tungsten in the deposit increases with the current density (table 3). This is to be expected, as under most conditions tungsten behaves as the less noble of the two metals. In the citrate solution at low current densities a relatively higher proportion of tungsten is obtained in the deposit than in other baths, and in this particular case an increase in the current density does not significantly increase the tungsten content of the deposit.

Temperature.—The composition of the deposit does not vary significantly with temperature (table 4), but the cathode efficiency improves considerably as the temperature is raised.[2] The main objection to deposits obtained at low temperatures is that their physical properties are inferior to those obtained above 90° C, as they are dark in color and unsound. On stripping the base metal away from them, they showed the presence of many cracks and usually fell to pieces. Table 17 shows that such deposits have more oxide inclusions than the deposits obtained at 90° C. Because of these disadvantages, most of the tungsten alloys were deposited from hot solutions.

Type of Organic Acid.—The organic acids vary in their capacity to bring about codeposition of tungsten. The following summary shows that gluconic acid yields deposits with the lowest tungsten content and citric acid the highest.

Acid	Approximate tungsten in deposit		
	(W/Co in bath=1)		(W/Co in bath=2)
	2 amp/dm²	5 amp/dm²	2 amp/dm²
	Percent	*Percent*	*Percent*
Gluconic	3	8	10
Malic	10	15	24
Hydroxyacetic			21
Tartaric	18	26	25
Citric	40	40	40

Concentration of Organic Salts.—Not enough data are at hand to determine accurately the effect of the concentration of the organic salt on the composition of the deposit. The effect seems to be small in the tartrate bath (see experiments 12 and 13; 14 and 15; table 2).

Total Concentration of Cobalt and Tungsten.—The content of tungsten in the deposit should increase as the content of cobalt and tungsten of the bath decreases (the W/Co ratio and current density being kept constant), because in the dilute bath the current density is nearer to its limiting value at which the maximum percentage of tungsten in the deposit is obtained. The total metal content of cobalt and tungsten, however, has only a minor role in affecting the composition of the deposit. Decrease in the metal content (cobalt and tungsten) of the bath slightly increases the tungsten content of the deposit from the gluconate bath (examples 44 and 45, table 2), but has no definite trend in the tartrate bath (examples 5 and 6; 8 and 9; 13 and 14; 17 and 18).

Concentration of Ammonium Salts.—As the baths are made alkaline by adding ammonia, which reacts with cobalt salt, some ammonium compounds are present before any further addition is made. Additional large amounts of ammonium salts slightly increases the percentage of tungsten in the deposit. (Table 2: Compare 3 and 4; 9 and 10, 16 and 17). Baths made up with ammonium salts of organic acids operate very much like those made with sodium or potassium salts.

[2] It is possible to compute the approximate cathode efficiency for most of these deposits without knowledge of their exact composition because the equivalent weights of W^{VI}, Co^{II}, Ni^{II}, and Fe^{II} are nearly the same.

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If ammonium compounds are entirely omitted from the plating solution (although the salt of the hydroxy acid is present at a pH of 8 to 9) the solubility of cobalt and tungsten is reduced and the cathode current efficiencies are so low that the solutions are not suitable for electrodeposition. If the solution contains ammonium salts only, and the hydroxy acids are omitted, the solubilities of cobalt and tungsten are also low, and the cathode current efficiencies are poor. However, as an exception, the ammoniacal ammonium sulfate solution yields fairly good deposits and is nearly practicable.

pH *of the Bath.*—No systematic study was made of the effect of the pH of the solution on the composition of deposit, because at the temperature of operation, loss of ammonia made it impracticable to keep the pH much above 9 for any length of time. In the presence of an excess of ammonia, at a temperature of 90° C, the pH was stable between 8.5 and 9. A pH lower than 8.0 resulted in increased precipitation of cobalt compounds from the solution on cooling.

Baths Containing Trivalent Cobalt.—Simple compounds containing cobalt in the trivalent state are not stable, but stable complexes containing Co^{III} are common, particularly in alkaline solutions. A test was made to determine whether a cobalt solution made up with Co^{III} would behave differently from Co^{II}, and in what state of oxidation the Co would be after a plating solution had been operated for some time. The presence of Co^{III} was shown by treating the solution with potassium iodide, acidifying with hydrochloric acid, and then heating in a closed container. This heating was necessary because the cobalt-ammines do not readily decompose when acidified. The liberated iodine was titrated with thiosulfate. The determination of cobalt in an oxidized ammoniacal solution by this method was quantitative; but this may not have been true in the analysis of the plating solutions, which contained organic constituents.

A cobalt-tungsten plating solution containing Co^{III} (made by oxidation of Co^{II} with H_2O_2 in ammoniacal solution) and Rochelle salt gave deposits very similar in composition and properties to those obtained from the corresponding cobaltous solution. After operation for some time, the cathode efficiencies based on Co^{III} rose to 120 percent, which indicates that some of the Co^{III} had been reduced. Conversely, operation of the cobaltous alloy plating solution, especially with air agitation, resulted in the formation of a small amount of trivalent cobalt.

A similar comparison was made between cobaltous and cobaltic alloy plating solutions made from ammoniacal solutions of ammonium sulfate and containing no organic constituents. There was no difference either in the operation of the plating solutions or in the type of deposit obtained. Therefore it is concluded that the valence of cobalt in the bath is of no practical importance.

Operation and Control of the Plating Process.—The cobalt-tungsten plating baths were operated in the manner of any ordinary plating bath. The potential required was about 1 v in a bath where the distance between anode and cathode was about 5 cm. Copper was not very satisfactory for suspending objects in the solution and for use as bus bars, because it corroded in the ammonia vapors and copper compounds dropped into the bath, and contaminated it. Nickel or nickel-plated metal should be used above the bath.

Containers for Plating Solutions.—All of the plating was done in glass vessels. Enamel-lined steel or ceramic tanks also are suitable. Stainless steel tanks may be suitable if the walls are shielded with glass plates. There was some attack on stainless steel immersion heaters, possibly as the result of electrolytic corrosion. Polyethylene can be used to line a tank, but not Saran, which slowly deteriorates in the solution.

Anodes.—Tungsten, cobalt, or a cobalt-tungsten alloy can be used as anodes. Tungsten is the most satisfactory anode, because it corrodes cleanly and smoothly with 100-percent current efficiency. It does not introduce any appreciable amount of insoluble matter into the bath, and the deposits are smooth even though the tungsten anodes are not covered with bags. The area of the tungsten anodes should be not less than about one-third of the cathode area, because otherwise the anodes may become passive. Higher anodic current densities can be used if mildly agitated with air.

When cobalt anodes are used, low anodic current densities should be employed, preferably under 1 amp/dm^2, because otherwise the anodes do not corrode well. At higher current densities, a gelatinous pink precipitate forms over the anode and may become detached and suspended in the

bath. With cobalt anodes under the best conditions, the deposits are not as smooth as with tungsten anodes. Enclosing the cobalt anodes in glass cloth bags yields smoother deposits, but circulation of the solution around the anodes is curtailed, and the bag gradually fills up with a pink precipitate. If cobalt anodes are used, it is more satisfactory to use no anode bags, and to depend on continuous filtration to clarify the bath.

Anodes of a cobalt-tungsten alloy containing 10 to 20 percent of tungsten operate satisfactorily, but anodes of this kind are not commercially available. A bath can be operated with a dual system of tungsten and cobalt anodes, if it is desired to maintain the composition of solution within close limits. For plating the interior of objects, anodes of tungsten or of cobalt-tungsten alloy may be used, but cobalt anodes are not suitable for the above reasons.

If a bath is operated with tungsten anodes, the concentration of tungsten in the solution increases, and eventually it becomes necessary to remove the excess. No convenient chemical method of precipitating tungsten from the alkaline solution was found. In a process occasionally used by us, the bath was electrolyzed with cobalt anodes at a temperature of about 50° C (to reduce evaporation and loss of ammonia), at a high-current density, until the excess of tungsten had been replaced by cobalt. On a large scale, the waste cathode deposit thus obtained could subsequently be used as an anode.

Insoluble anodes should not be used in these baths, because the oxidation of the organic constituents at the anode produces deleterious products. After a bath has been operated for some time with insoluble anodes, for example of platinum, the deposits become brighter and more stressed, and pitting, cracking and exfoliation may occur. Filtration through activated charcoal improves the condition of the solution but does not entirely remove the deleterious products.

Control of Ammonia Content.—The most inconvenient feature of these plating solutions is the large loss of water and ammonia at the elevated temperatures employed. These losses were replaced by adding a mixture of ammonium hydroxide and water (1:1) to keep the solution level constant. No other control of the ammonia content of the solution was required. Bubbling of ammonia gas through the bath was tried but did not prove advantageous. On a large scale it might be practicable to partially enclose the system to reduce the loss of ammonia. In an effort to reduce the loss of water and ammonia, rods and sheets of plastic were floated on the surface, in the manner frequently used for cutting down the spray losses in chromium plating, but this procedure had no effect in reducing the losses from the bath. One method that practically prevented evaporation consisted of floating a layer of melted paraffin, about 1 cm thick, on the surface. If the objects to be plated were clean, wet, and free from water-break, they could be introduced into the bath through the paraffin layer without any of it adhering sufficiently to prevent plating. On continued operation of the bath, pitting of the deposits began to occur, but this was not necessarily caused by the paraffin. Further consideration of the use of a molten layer over the bath seems warranted.

An effort was made to substitute some less volatile organic amines for ammonia. Four were tried, but the preliminary results were not encouraging. Data on these amines are given in table 5. Only one, hydroxyethylethylenediamine, yielded a high cathode efficiency. The deposits from all the solutions containing amines were inferior, and fell to pieces when the base metal was stripped away. Some amines, for example, guanidine and hydrazine, completely precipitated the cobalt from the alkaline tartrate solution.

Pretreatments for Plating—Methods of Securing Adhesion—Most of the plating was done on steel, although there was no difficulty in plating on copper and brass. Any of the commonly accepted methods of cleaning the metals can be used.

When steel, particularly high-carbon steel, was directly plated in the bath, a high degree of adhesion was not obtained, and it was necessary to study this troublesome problem. The adhesion was measured qualitatively by plating 0.25 mm or more of the deposit on a steel rod and then attempting to detach the deposit by mechanical means, such as twisting or bending the rod until it broke. The use of etches and strikes alone did not improve the adhesion. A fair degree of adhesion was obtained by first plating the steel with cobalt, and then slightly etching the cobalt anodically with reverse current in the alloy plating bath. The best adhesion was obtained by

TABLE 5.—*Deposition of cobalt-tungsten alloys from solutions containing organic amines*

Composition of bath:	g/liter
Cobalt	15
Tungsten	10
Rochelle salt	100

Amine as indicated.
Temperature 90° C
pH, 8.5

No.	Amine			Cathode efficiency—		Tungsten in deposit—	
	Type	Concentration		2 amp/dm²	5 amp/dm²	2 amp/dm²	5 amp/dm²
		Molarity	g/liter				
				Percent	*Percent*	*Percent*	*Percent*
1	Ethanolamine	0.80	50	39	20	24	
2	Tetra-ethanol-amine ammonium hydroxide	.20	50	26	7	21	
3	Ethylenediamine	.30	18	26	60	13	
4	Hydroxyethylethylenediamine	.35	35	80	97	15	

the following process, in which alternating current was used in the final step.

Anodic Etch.—After the steel had been cleaned by any suitable process, it was anodically etched in 70 percent sulfuric acid for 2 minutes at a current density of 25 amp/dm², and rinsed.

Cobalt Strike.—The steel was plated with cobalt for 3 minutes at a current density of 20 amp/dm² in a solution which contained cobalt, 20 g/liter and HCl to produce a pH of 0.5.

Treatment with alternating current.—After rinsing the object, preferably with 1:1 hydrochloric acid, it was transferred to the plating solution, and alternating current of 0.25 amp/dm² was passed through the work for 5 to 15 seconds, and then the direct current was immediately turned on.

With this process the adhesion was satisfactory, and a deposit 0.25 mm thick could not be separated from the base metal by any mechanical means. As alternating current had not previously been utilized for securing adhesion, some further study was made of it, but only the facts pertinent to this alloy system will be mentioned here. The amount of alternating current required for securing good adhesion could be varied over a moderate range, but to some extent it depended on the composition of the bath. Baths low in tungsten but high in cobalt (for example Co 50 g/liter), required more critical control of the amount of alternating current, for example, smaller amounts of alternating current had to be employed than in dilute bath. If the alternating current was too high, for example 1 amp/dm² or more, or if the time of treatment was too long, poor adhesion resulted. Within certain limits, higher current densities of alternating current could be used if the time of treatment was correspondingly reduced.

It is important to secure good adhesion of the initial cobalt layer to the steel, otherwise it would be useless to secure a high degree of adhesion of the alloy to the cobalt layer. Good adherence of cobalt to steel (particularly to steel containing 0.5% or more of carbon), could not be consistently obtained from the standard cobalt plating baths, whether they were made up from chloride or sulfate. No mention of this difficulty is found in the literature. Steps 1 and 2 of the above process provide satisfactory adhesion of cobalt to steel, and both steps are necessary.

Effect of Impurities on the Operation of the Bath.—The alloy plating solution is not very sensitive to the metallic impurities that might become introduced in a plating room. The effects of impurities were determined by adding small amounts of them to the solution containing: cobalt, 25 g/liter; tungsten, 25 g/liter; and Rochelle salt, 400 g/liter. The addition of copper, 0.2 g/liter resulted in the production of a bright deposit, but larger amounts yielded a nodular or spongy, dark deposit. Zinc had little effect on the deposit when added in quantities up to 10 g/liter, and tin likewise had no deleterious effect on the deposit, but caused a precipitate to form in the bath when its concentration became as high as 25 g/liter. Spectrochemical examination of the deposits obtained from the solutions contaminated with zinc and tin showed the presence of moderate amounts of

those metals, which, however, may have been present as basic inclusions. Lead caused uneven plating if present in concentrations higher than 0.2 g/liter; and if present to the extent of 5 g/liter, lead plated out of the solution more readily than the alloy. Addition of 0.2 g/liter of cadmium caused a lowering of the cathode efficiency, and in larger concentrations it produced spongy deposits similar to those obtained with copper. Iron did not affect the deposit when present to the extent of 5 g/liter, but caused a gradual precipitation of iron compounds from the solution. Chromic acid had no appreciable effect when added in small quantities, but when present to the extent of 5 g/liter, plating ceased. However, after the hot solution had stood for several hours, the chromic acid was reduced and the bath operated satisfactorily once more. Small quantities of sodium cyanide (1 g/liter) had no effect, but 5 g/liter produced a precipitate.

Plating with Alternating Current Superimposed on Direct Current.—Some deposits were plated using both direct current and 60-cycle alternating current in different ratios. The resultant current was pulsating direct current except when a high proportion of alternating current was used, in which case there was a momentary reversal of current at the cathode. The deposits produced with the mixed alternating and direct currents had about the same composition as those obtained with direct current alone and were similar in appearance. No obvious advantage was found from superimposing the alternating current.

Stress in Deposits During Deposition.—Attempts were made to produce thick separable deposits on a surface upon which the alloy would not be strongly adherent, for example on lead, to determine the feasibility of using the alloy for electroforming. When the alloy became more than 0.5 mm thick, it tended to crack spontaneously, although this did not occur when the alloy was plated adherently on steel. The stress developed during plating was qualitatively measured with a contractometer and was found to be slightly less than that occurring in an ordinary acid-cobalt bath, but slightly greater than that occurring in a Watts nickel bath. These few measurements did not throw light on the cause of the cracking.

Stability of Plating Solutions.—The alloy plating solutions used in the investigation were chiefly the Rochelle salt baths, which were fairly stable. A bath of a few liters was operated for a period long enough to deposit an amount of cobalt equal to that initially present, without showing signs of deterioration. When these solutions are allowed to stand uncovered, they gradually lose ammonia, and a pink solid precipitates, and redissolves in the bath only slowly with the addition of ammonia and the application of heat. Therefore the baths should be kept covered when not in use.

3. Electrodeposition of Nickel-Tungsten Alloys

Literature.—As more work has been reported on the nickel-tungsten alloys than on the other tungsten alloys, a more detailed discussion is desirable. Fink and Jones [13] used a carbonate solution for the electrodeposition of a nickel-tungsten alloy, and obtained deposits that were only a few microns thick. Our experience with the plating bath of Holt and Nielson [17], which consisted of a solution of nickel sulfate and sodium tungstate at a low pH, was that the deposits were low in tungsten, usually not over 7 percent, and that deposits over 0.025 mm thick were rough. The numerous patents of Armstrong and Menefee [1 to 8] make broad claims for other metals and operating conditions, but limit their examples to the codeposition of nickel-tungsten alloys from baths with a pH below 7, which contain, in addition to the alloying metals, fluorides, phosphates, borates, citrates, and ammonium salts. The deposits that were obtained by their process were not any sounder than those plated from the simpler solution of Holt and Nielson; but higher tungsten contents could be obtained. Although the importance of fluorides in these baths is emphasized, neither fluorides, borates, or phosphates appear to be of any value. The deposits from the ammoniacal solution recommended by Goltz and Kharlamov [14] contained 20 percent of tungsten, and were hard, but because of the excessively high current density used (20 to 40 amp/dm^2), the deposits were porous and cracked. If their solution is electrolyzed at a current density of 2 amp/dm^2, a deposit is obtained that is lower in tungsten but much sounder. As the recently published paper of Vaaler and Holt [25] described plating conditions similar to those that are reported here, its discussion will be presented later in this paper.

Less emphasis has been put on the nickel-

tungsten than on the cobalt-tungsten system, because the cobalt alloys show a wider range of properties, can be obtained with higher percentages of tungsten, and exhibit precipitation-hardening to a greater extent than the nickel alloys.

Solubility Relations.—Plating solutions containing hydroxy-acids and ammonium salts, similar to those used for the cobalt alloys, were used for depositing the nickel alloys. The tartrate and citrate solutions were the most satisfactory. Solubility experiments showed less constancy of the solubility product of nickel and tungsten than of the cobalt and tungsten, but this relation serves as a convenient indicator of the solubility relations in a variety of solutions, as shown in table 6.

TABLE 6.—*Solubility relations of nickel and tungsten in ammonical solutions at pH 8.5*

[The citrate and tartrate solutions contained 50 g/liter of ammonium chloride]

Salt			Solubility product	
Type	Concentration		NiXW	CoXW
	Molarity	g/liter	g/liter	g/liter
Rochelle	1.4	400	3,000	.....
Ammonium tartrate	.7	125	4,000	.....
Do	1.4	250	6,000	.....
Ammonium citrate	.8	200	2,500	.....
Do	1.6	400	5,000	.....
Ammonium sulfate	2.3	300	.....	.....
Sodium hexa-metaphosphate	.3	200	2,500	0
Ammonium sulfamate	2.0	230	1,600	75
Ammonium acid phosphite	1.2	120	1,100	42
Ammonium fluoborate	1.9	200	170	0
Ammonium bifluoride	3.5	200	160	10

In general, the mutual solubilities of nickel and tungsten in the electrolyte were greater than the mutual solubilities of cobalt and tungsten. For example, in an ammonium tartrate solution containing tungstate, the concentration of nickel may be as high as 100 g/liter, whereas that of cobalt cannot be much above 50 g/liter without eventually precipitating. The solubility products of nickel and tungsten in the solutions containing only inorganic salts are much higher than for cobalt and tungsten, and indicate a greater possibility of preparing an inorganic bath for the nickel than for the cobalt alloy. Some data for the latter are given in table 6 for comparative purposes. The large solubility product of nickel and tungsten in the hexametaphosphate solution is noteworthy.

D. *Factors Affecting the Composition of the Deposit.*—Nickel alloys could not be obtained with as high a content of tungsten as the cobalt alloys. The limit of the tungsten content in the nickel alloys was about 35 percent, as compared with about 50 percent for the cobalt-tungsten alloys. The effects of the variables of bath composition and operating conditions were similar to those observed with the cobalt system, and hence the discussion of this subject can be abridged except where the two systems differ. The relations of the composition of the plating solutions and of the deposits are illustrated in table 7; and the effects of current density in table 8. Most of the data were obtained with solutions of citrates and tartrates, the latter solution producing the soundest deposits.

The main conclusions are as follows:

1. The tungsten-nickel ratio of the bath (fig. 2 and fig. 3) has the most important effect on the

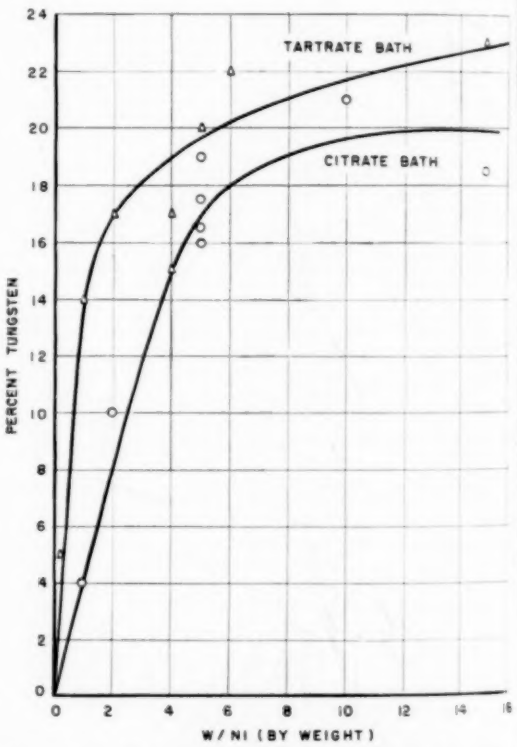

FIGURE 2.—*Effect of tungsten-nickel ratio on the percentage of tungsten in the deposit from ammonium tartrate and sodium citrate alloy baths of various compositions at a current density of 2 amp/dm².*

TABLE 7.—*Composition of nickel-tungsten alloys deposited from ammoniacal solutions of organic salts*

[Each solution contained 50 g/liter of ammonium chloride; temperature 90° C; pH 8.5]

No.	Bath composition								Cathode efficiency—		Tungsten in deposit—	
		Ni		W		Organic salt						
	W/Ni (weight)	Molarity	g/liter	Molarity	g/liter	Type	Concentration		2 amp/dm²	5 amp/dm²	2 amp/dm²	5 amp/dm²
							Molarity	g/liter				
CITRATE												
									Percent	*Percent*	*Percent*	*Percent*
1	1	0.68	40	0.20	35	Na	0.60	200	81	81	4	9
2	2	.34	19	.20	35	Na	.30	100	95	77	10	15
3	3	.11	7	.19	17	Na	.30	100	.....	80	.....	25
4	4	.42	25	.54	100	NH_4	1.60	400	61	64	12	12
5	5	.11	7	.20	35	Na	0.30	100	88	63	16	26
6	5	.11	7	.20	35	Na	.65	230	47	63	17	26
7[a]	5	.21	13	.37	68	Na	.60	200	88	86	16	31
8[b]	5	.11	7	.20	35	Na	.30	100	75	53	19	25
9	10	.11	7	.37	68	Na	.30	100	81	81	21	29
10	15	.11	7	.52	95	Na	.30	100	97	96	18	26
TARTRATE												
11	0.2	0.42	25	0.03	5	NH_4	1.30	245	95	96	5	5
12	1	.42	25	.13	25	NH_4	1.30	245	94	.....	14	.....
13	1	.68	40	.20	35	Na, K	0.70	200	.....	95	[c] 7	5
14	2	.42	25	.27	50	NH_4	1.30	245	89	.....	17	.....
15	4	.42	25	.54	100	Na, K	1.40	400	90	92	9	13
16	4	.42	25	.54	100	NH_4	0.65	120	60	84	15	20
17	4	.42	25	.54	100	NH_4	1.30	245	80	77	17	21
18	5	.08	5	.13	25	NH_4	1.30	245	55	52	21	26
19	6	.34	20	.63	115	NH_4	1.30	245	75	.....	22	.....
HYDROXYACETATE												
20	0.3	1.70	100	0.16	30	K	2.5	300	.....	.....	4	5
21[a]	.3	1.70	100	.16	30	K	5.0	600	.....	.....	.....	1
22	.3	0.85	50	.08	15	NH_4	2.5	250	.....	100	.....	2
23	.6	.85	50	.16	30	NH_4	5.0	500	.....	.....	.....	13
24	4	.42	25	.54	100	NH_4	5.0	500	98	76	17	21
SACCHARATE												
25	0.30	0.85	50	0.08	15	K, H	1.6	400	.....	[c]	8	7
26	.6	.85	50	.16	30	K, H	1.6	400	.....	[c]	13	.....
GLYCINATE												
27	0.3	1.7	100	0.16	30	K	2.7	300	90	.....	5	11
INORGANIC												
28[d]	0.4	0.3	18	0.04	8	.....	.....	.....	.....	.....	10	14

[a] Bath contained NH_4Cl, 100 g/liter.
[b] Bath contained NH_4Cl, 200 g/liter.
[c] 3 amp/dm².
[d] Bath contained $(NH_4)_2SO_4$, 400 g/liter.

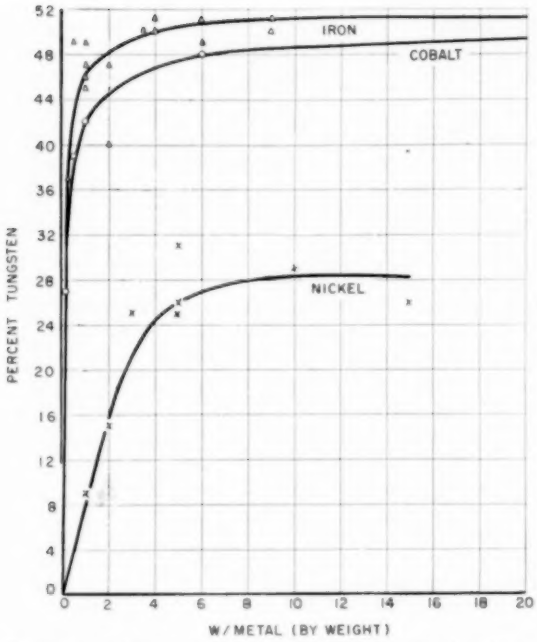

FIGURE 3.—*Comparison of effect of tungsten-metal ratio on the percentage of tungsten in the deposit plated from nickel, cobalt, and iron-tungsten alloy citrate baths of various compositions at a current density of 5 amp/dm².*

composition of the deposits. When this ratio exceeds 4, the increase of tungsten in the deposit is slight. In no instance was a deposit obtained (as was the case for the cobalt alloy) in which the ratio of tungsten to nickel was higher in the deposit than in the bath.

2. The content of tungsten in the deposit increases with current density (table 8). It will be recalled that in the citrate cobalt-alloy solution the composition of the deposit was almost unaffected by variations of current density. This behavior is not shown by the citrate nickel-alloy plating solution. The deposits obtained from tartrate and other solutions at a current density of 5 amp/dm² were not as sound as those obtained at a current density of 2 amp/dm², and usually developed cracks when the copper supporting tube was stripped away. It has not been determined whether this cracking is related to the composition of the deposit or to the precipitation of inclusions at the higher current density.

3 The type of organic acid employed (if any) has very little effect on the composition of the deposit, in contrast to the cobalt alloy systems in which considerably more tungsten is codeposited from a citrate solution than from any other.

TABLE 8. *Effect of current density on the composition of nickel-tungsten alloys*

[Each solution contained ammonium chloride, 50 g/liter. Temperature 90° C; pH 8.5.]

No.	Bath composition						Current density	Cathode efficiency	Tungsten in deposit
	W/Ni (weight)	Ni		W		Sodium citrate concentration			
		Molarity	g/liter	Molarity	g/liter	Molarity	g/liter			
								amp/dm²	*Percent*	*Percent*
1	1	0.68	40	0.20	35	0.6	200	2	81	4
2	1	.68	40	.20	35	.6	200	5	81	9
3	1	.68	40	.20	35	.6	200	10	----------	15
4	2	.34	19	.20	35	.3	100	2	95	10
5	2	.34	19	.20	35	.3	100	5	77	17
6	2	.34	19	.20	35	.3	100	10	88	18
7	2	.34	19	.20	35	.3	100	20	82	28
8	2	.34	19	.20	35	.3	100	30	93	27
9	5	.22	13	.37	68	.6	200	2	88	11
10	5	.22	13	.37	68	.6	200	5	86	31
11	5	.22	13	.37	68	.6	200	10	79	37
12	5	.22	13	.37	68	.6	200	20	82	35
13	5	.22	13	.37	68	.6	200	30	51	32
14	15	.11	7	.52	95	.3	100	2	97	18
15	15	.11	7	.52	95	.3	100	5	96	26
16	15	.11	7	.52	95	.3	100	10	94	37
17	15	.11	7	.52	95	.3	100	20	62	38

Summary from Table 7.—Effect of type of plating solution on the composition of nickel-tungsten alloys.

Ni, 25 g/liter; W, 100 g/liter

Type of plating solution	W in deposit	
	2 amp/dm²	5 amp/dm²
	Percent	*Percent*
Na-K tartrate	9	13
Ammonium tartrate	15	20
Citrate	14	16
Hydroxyacetate	17	21
Inorganic solution	10	14

4. From data available, it does not appear that variations in the concentration of the salts of organic acids or in the total concentration of nickel and tungsten have any important effect on the composition of the deposit.

5. As with the cobalt system, the addition of ammonium salts up to several hundred grams per liter to the baths, which already contain ammonium compounds as made up, has little effect on the deposits except to darken the color. Alkaline plating solutions prepared from salts of the hydroxy acids, with no ammonium compounds present, operate very poorly. The mutual solubility of nickel and tungsten is much reduced, and the cathode efficiency is only a few percent. Addition of a small amount of ammonium compounds raises the efficiency to 90 percent. However, an ammonia-free citrate plating solution, which initially had a very low cathode current efficiency, improved considerably in this respect after being used for several hours.

Solutions containing inorganic ammonium salts and no salts of hydroxy acids do not operate as well as the preferred type of bath, because of the lower solubility of the metals and the lower cathode efficiency. These solutions are, however, much more satisfactory than those containing hydroxy acids but no ammonium salts. As compared with the preferred type of bath, they have the advantage that an insoluble anode can be used in them.

In the tartrate bath a difference was noted in the composition of the deposits (12, 13, 15, and 17 in table 7) according to whether the solution was made up with Rochelle salt or with ammonium tartrate. From the latter solution the deposits contained significantly more tungsten. This effect is not caused by the presence of a larger quantity of ammonium salts, as adding large quantities of ammonium salts to the Rochelle salt solution did not effect the composition of the deposits. It may be caused by the presence of the sodium or potassium salts, though it is rather unusual for inert ions such as these to influence the composition of an alloy deposit.

Comparison with Work of Vaaler and Holt.—It is of interest to compare the above observations with those of Vaaler and Holt [25], who worked mainly with citrate solutions. Their range of compositions of baths and alloys and their operating conditions are similar to those reported here. The main difference is that they used temperatures only up to 70° C, whereas the best quality of deposit was obtained in the present work at higher temperatures. Occasionally they used insoluble anodes, which form deleterious products in the bath and produce bright, strained, and pitted deposits. Current densities of 7 to 15 amp/dm², such as they used, are too high for the production of deposits sound enough for commercial use.

Operation of Plating Solutions.—Much of what has been said in regard to the control of the temperature, pH, ammonia content, anodes, and adhesion in cobalt-tungsten alloy solutions applies to the nickel-tungsten alloy solutions. The anode corrosion of nickel in these baths is poorer than that of cobalt, and the anode current density can not exceed 0.3 amp/dm², without forming a precipitate on the anode. The effects of many impurities in the solution have not been studied, but small amounts of copper produce a bright deposit and larger quantities, a rough, dark deposit. The nickel-alloy solutions have less tendency than the cobalt-tungsten solutions to precipitate on long standing.

4. Electrodeposition of Iron-Tungsten Alloys

General.—Our knowledge concerning the iron-tungsten plating solutions is less complete than that for the other two alloys, because the former are more difficult to investigate. The iron-tungsten alloy systems exhibit considerable differences from those of cobalt and nickel alloys. In some respects, this is the most interesting of the three systems studied, because the tungsten contents of the deposits are higher, and because some of the deposits are harder even than chromium.

One of the main difficulties involved in the plating solutions for the iron-tungsten system is

that the iron can exist in two states of oxidation. Plating is more readily carried out in the solutions of Fe II than of Fe III, but the alkaline solutions of ferrous compounds oxidize rapidly in the air. Hence, it is not practicable to know exactly the composition of a bath that has been in operation for some time. Because the solubilities of the iron-organic complexes are not as high as those of cobalt and nickel, a wide range of concentrations is not feasible. The cathode efficiencies are lower, for example, about 50 percent. This situation increased the difficulty of plating thick deposits for physical examination.

Solubility Relations of the Iron-Tungsten Plating Solutions.—No quantitative solubility studies were made on the iron-tungsten plating solutions, as was done for the nickel and cobalt solutions. Ferric compounds had a higher solubility than ferrous compounds. In the citrate bath maximum concentrations of about 25 g each of iron and tungsten could be obtained but the solutions were not as stable as the corresponding nickel and cobalt solutions, and iron tungstates gradually precipitated on operation. The tartrate solutions were not satisfactory because of the low solubility of ferrous compounds in them.

In making up the alloy plating solution, precipitation was likely to occur if the salts were not dissolved in the right order. The citrate, iron sulfate, and the ammonium salts were dissolved successively, and the solution was made ammoniacal. The tungstate was dissolved separately and was made ammoniacal before adding it to the iron solution.

Factors Affecting Composition of Deposit.—The outstanding characteristic of the deposition of iron-tungsten alloys is that, despite large changes in the composition of the plating solution and the conditions of operation, the deposit maintains a fairly constant composition, with about 50 percent of tungsten. This behavior is illustrated in tables 9 and 10 and figure 3 in which all of the deposits contain between 30 and 60 percent of tungsten, and most of them between 40 and 55 percent. It has not proved expedient to produce low-tungsten alloys because of the difficulty in controlling the small concentration of tungsten that is required in the plating solution.

As the composition of the deposit does not vary greatly with a change of variables, no detailed analysis of these effects is included, particularly because the reproducibility of the composition of the deposits was not very high. The range of variations is shown in tables 9 and 10. The only condition that made a decided change in the composition of the deposit was the use of a malate solution (table 9) that yielded deposits containing about 30 percent of tungsten, as compared with 45 or 50 percent for the citrate solutions. The gluconate and tartrate solutions yielded deposits with about the same composition as did the citrate. The tartrate solution is not satisfactory because iron tartrates gradually precipitate from it on heating.

In the iron-tungsten system, the tungsten usually behaves as the less noble metal, that is, the metal ratio, W/Fe, of the deposit was usually smaller than that of the solution. As with the cobalt-tungsten alloys, however, certain of the plating solutions yielded deposits that had a larger ratio than the solution, thus indicating a reversal of the relative potentials of the co-deposited metals. This is illustrated by No. 1 table 9 where the metal ratio of the deposit is and that of the solution is 0.5, and by No. 17 table 9, where the metal ratio of the deposit is 0.5, while that of the solution is 0.2. This apparent shifting of the deposition characteristic of tungsten is shown with both cobalt and iron only in solutions with a low concentration of tungsten. If more tungsten is added to a solution, the tungsten content of the deposit approaches a limit, while the metal ratio of the solution increases and soon exceeds the maximum that the deposit is capable of attaining.

The main effect of the composition and operating conditions of the solution is upon the cathode current efficiency. Ferrous solutions [13 to 22] have cathode efficiencies of 65 to 85 percent, and ferric solutions [1 to 14] of 30 to 50 percent. Increasing the citrate content materially lowers the cathode efficiency [compare 3 and 4; 7 and 8; 11 and 13; 20 and 21]. The cathode efficiency (table 10) at 50° C is considerably lower than at 70° and 90° C.

Operation of Plating Solutions.—The operation of the ferrous solutions was not satisfactory because they tend to oxidize readily. By using a deep vessel and passing a slow stream of carbon dioxide over the solution, oxidation could be retarded. In solutions operated in the air, 50 percent or more of the iron became ferric. On standing, the solu-

TABLE 9.—*Composition of iron-tungsten alloys deposited from ammoniacal solutions*

Each solution contained additional ammonium salts, 50-100 g/liter, unless otherwise indicated. Baths were operated at a pH of 8.5 to 9, and above 90° C]

No.	Bath composition								Cathode efficiency			Tungsten in deposit		
		Fe		W		Organic salt								
	W/Fe (weight)	Molarity	g/liter	Molarity	g/liter	Type	Concentration		2 amp/dm²	5 amp/dm²	10 amp/dm²	2 amp/dm²	5 amp/dm²	10 amp/dm²
							Molarity	g/liter						
						FERRIC CITRATE BATH								
									Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1	0.5	0.14	8	0.02	4	Na	0.30	100	47	29	.....	.....	49	55
2	1.0	.14	8	.04	8	Na	.30	100	53	40	.....	53	.....	.....
3	2.0	.27	16	.20	35	Na	.30	100	.....	43	.....	.....	47	48
4	2.0	.55	32	.40	70	Na	.60	200	.....	15	.....	.....	40	.....
5	3.0	.21	12	.20	35	Na	.30	100	46	38	.....	51	46	.....
6	3.5	.14	8	.15	28	Na	.30	100	.....	47	.....	.....	50	.....
7	4.0	.14	8	.20	35	Na	.30	100	.....	58	21	.....	50	52
8	4.0	.14	8	.20	35	Na	.85	300	.....	.....	11	.....	.....	45
9	6.0	.14	8	.27	50	Na	.30	100	.....	47	.....	.....	49	.....
10	6.0	.10	6	.20	35	Na	.30	100	.....	40	.....	.....	51	.....
11	9.0	.14	8	.40	72	Na	.30	100	.....	42	.....	.....	51	.....
12	9.0	.07	4	.20	35	Na	.30	100	.....	29	20	.....	50	.....
13	9.0	.14	8	.40	70	Na	.60	200	.....	23	.....	.....	50	.....
14	175	.003	0.2	.20	35	Na	.30	100	.....	12	.....	.....	63	.....
						FERROUS CITRATE BATH								
15 [a]	.....	0.43	25	.....	.....	NH_4	0.40	100	82	.....	57	.....	.....	.....
16 [a]	.....	.43	25	.....	.....	NH_4	.80	200	.....	.....	45	.....	.....	.....
17	0.2	.43	25	0.03	5	NH_4	.40	100	66	78	75	33	37	47
18 [b]	1.0	.43	25	.14	25	NH_4	.40	100	[c] 85	87	67	47	47	49
19 [c]	1.0	.43	25	.14	25	NH_4	.40	100	87	73	.....	46	46	.....
20	1.0	.43	25	.14	25	NH_4	.40	100	69	73	.....	35	45	.....
21	1.0	.43	25	.14	25	NH_4	.80	200	.....	17	21	.....	49	50
22	4.0	.43	25	.54	100	NH_4	.80	200	.....	15	14	.....	51	57
						FERRIC GLUCONATE BATH								
23	3.5	0.17	10	0.20	35	NH_4	0.50	110	29	40	.....	[c] 41	41	.....
						FERRIC MALATE BATH								
24	1	0.43	25	0.14	25	NH_4	1.5	250	.....	21	52	.....	28	.....
						FERROUS MALATE BATH								
25	1	0.43	25	0.14	25	NH_4	1.5	250	52	77	83	29	30	34
						FERRIC TARTRATE BATH								
26	4	0.14	8	0.20	35	NH_4	0.5	100	.....	44	.....	.....	35	.....
						FERROUS TARTRATE BATH								
27	1	0.14	8	0.20	35	NH_4	0.5	100	.....	42	.....	.....	57	.....

[a] Iron plating bath. Contained no tungsten.

[b] Bath contained $(NH_4)_2SO_4$, 100 g/liter.

[c] 3 amp/dm².

[d] Bath contained $(NH_4)_2SO_4$, 300 g/liter.

tions were entirely converted to ferric and were difficult to reduce again. One advantage of the ferrous solution is that the cathode efficiencies are higher and the yields are greater for the same cathode efficiency. Deposits can be obtained at lower current densities in the ferrous solution than in the ferric, in which the current density usually must be at least 5 amp/dm.^{2}

Iron or tungsten anodes may be used. Neither was entirely satisfactory, because they tended to become passive unless either a large excess of citrate was present, or a low anode current density was used.

4. Electrodeposition of Ternary Alloys of Tungsten

Some ternary alloys containing nickel, cobalt, and tungsten; and iron, cobalt, and tungsten, were deposited to demonstrate that the process is feasible, but no detailed study of their deposition or properties was made. The data given in table 1

TABLE 10.—*Effect of temperature on the composition of iron-tungsten alloys deposited from citrate solutions*

[Each solution contained ammonium chloride, 50 g/liter. Current density 5 amp/dm^2, pH of plating solutions 8.5.]

No.	Bath composition							Current efficiency at—			Tungsten in deposit at—		
	W/Fe (weight)	Ferric		W		Sodium citrate concentration		50° C	70° C	90° C	50° C	70° C	90° C
		Molarity	g/liter	Molarity	g/liter	Molarity	g/liter						
								Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
1	2	0.29	16	0.20	35	0.20	100	29	48	43	37	41	
2	3	.21	12	.20	35	.30	100	19	37	38	41	52	
3	3.5	.14	8	.15	28	.30	100	34	44	47	48	45	
4	4.5	.14	8	.20	35	.30	100	.....	43	58	.....	46	
5	6.0	.11	6	.20	35	.30	100	.....	55	41	.....	46	
6	9.0	.07	4	.20	35	.30	100	11	38	29	61	53	
7	9.0	.14	8	.40	72	.30	100	26	.....	42	43	.....	
							Avg	24	44	42	46	47	
8	2.0	.57	32	.40	70	.60	200	.....	28	15	.....	47	
9	4.5	.14	8	.20	35	.20	70	.....	23	27	.....	53	
10	9.0	.14	8	.40	70	.60	200	.....	25	23	.....	49	

TABLE 11.—*Electrodeposition of ternary alloys of tungsten with the iron group metals from citrate solutions*

[Each solution contained additional ammonium salts, 50 g/liter. Baths were operated at a pH of 8.5 to 9.0 and a temperature above 90° C.]

No.	Bath composition												Current density	Current efficiency	Composition of deposit			
	W/Fe+Ni+Co (weight)	Co		Ni		Fe		W		Citrate					Co	Ni	Fe	W
		Molarity	g/liter	Molarity	g/liter	Molarity	g/liter	Molarity	g/liter	Type	Concentration							
											Molarity	g/liter						
	Ni–Co–W																	
													amp/dm^2		*Percent*	*Percent*	*Percent*	*Percent*
1	6.0	0.05	3	0.05	3	.....	.....	0.20	35	Na	0.30	100	3	97	26	48	.....	
2	6.0	.05	3	.05	3	.....	.....	.20	35	Na	.30	100	6	76	16	48	.....	
	Co–W–Fe																	
3	0.16	0.42	25	.....	.....	0.09	5	0.03	5	NH_4	1.60	380	2	72	74	.....	12	
4	.16	.42	25	.....	.....	.09	5	.03	5	NH_4	1.60	380	5	47	73	.....	14	
5	.16	.42	25	.....	.....	.09	5	.03	5	NH_4	1.60	380	10	49	73	.....	14	
6	.10	.42	25	.....	.....	.45	25	.03	5	NH_4	1.60	380	2	68	60	.....	23	
7	.10	.42	25	.....	.....	.45	25	.03	5	NH_4	1.60	380	5	55	58	.....	25	
8	.10	.42	25	.....	.....	.45	25	.03	5	NH_4	1.60	380	10	38	50	.....	33	

for the iron-cobalt-tungsten alloys show that the tungsten content of the deposit is lower than if a binary alloy had been deposited. For exmaple, a solution containing iron and tungsten would have yielded a deposit containing about 50 percent of tungsten, and one containing cobalt and tungsten a deposit containing about 25 percent of tungsten, but the ternary alloy contained from 14 to 17 percent of tungsten. Sykes [24] has shown that a metallurgical cobalt-iron-tungsten alloy containing 50 percent of Fe, 30 percent of Co, and 20 percent of W has a better hot-hardness than other compositions. The electrodeposition of such a ternary alloy may be of interest.

6. Defects of Deposits

The Rochelle salt and the citrate baths generally operated satisfactorily, but occasionally pitting and misplating (that is incomplete coverage of a surface) occurred from no known cause and no effective remedy was found. It was difficult to study these defects because the conditions could not be produced at will. The misplating was most likely to occur in the concentrated baths when low current densities were used. It could be almost entirely prevented by first coating the object with a cobalt strike and using an initially high current density in the alloy bath. The pitting of deposits could be lessened by moving of the object and by filtering of the solution through activated charcoal. Plating solutions containing high concentrations of hydroxyacetates were especially prone to pit. This is regrettable because this acid is the most economical for preparing the solutions for plating tungsten alloys.

7. Stripping Defective Deposits From Steel

Defective deposits of cobalt-tungsten alloy were stripped from steel anodically in either a cyanide solution or an ammoniacal solution of ammonium nitrate. The latter solution was almost saturated with ammonium nitrate and contained 100 to 200 ml of ammonium hydroxide per liter. The anodic current density was about 8 amp/dm^2. Although the stripping action in this bath was rapid, after the solution was used for a time, it tended to attack carbon steels. The cyanide solution contained sodium cyanide, 200 g/liter and the current density ranged from 1 to 5 amp/dm^2. At the lower current density, the metal was active and stripped with good efficiency, but at the higher current densities, the action was slower. The cyanide solution is more reliable than the nitrate when it is important not to injure the steel. Nickel-tungsten alloys can be anodically stripped from steel with a hot saturated solution of sodium or ammonium nitrate, in the same manner that nickel is stripped. The required current density is about 25 amp/dm^2.

To strip coatings from steel for analysis, a solution consisting of 2 volumes of fuming nitric acid and 1 volume of hydrofluoric acid is used, which rapidly dissolves the coating with very slight attack of the steel. The solution must be warmed on the steam bath until the reaction begins.

8. Analysis of Alloy Deposits and Plating Solutions

No high degree of accuracy was attempted in the analyses, as the results of the plating experiments were not highly reproducible. It was usually considered satisfactory to know the concentration of each metal in the plating solution within about 5 percent of its content, and the composition of the deposits to the nearest percent.

In analyzing for tungsten, the deposits were dissolved in nitric and hydrofluoric acid in the manner indicated above, and the solution was evaporated to fumes of sulfuric acid. The tungsten was precipitated with either brucine or cinchonine. The presence of the iron group metals did not interfere with the tungsten determination.

The analysis of the baths was a little more troublesome because of the presence of the organic matter. The tungsten was determined by boiling a portion of the solution with nitric acid and filtering off the tungsten, usually without the addition of an alkaloid, unless more precise results were desired. A higher degree of accuracy was obtained by destroying the organic constituents of the solutions before precipitating the tungsten.

A cyanide titration was occasionally used for determining cobalt [12] in the plating solutions. It was necessary first to destroy the hydroxy acid, as otherwise low results were obtained. The complete oxidation of the organic acid was indicated by no further charring when fumed with sulfuric acid. Oxidation did not proceed very fast with nitric and sulfuric acid. Better results were obtained by treating with potassium periodate and sulfuric acid and heating to fuming. With citrates, hot concentrated sulfuric acid and per-

sulfates were effective. Even after the organic acid was destroyed, the titration of cobalt gave results that were about 10 percent too high. For this reason a colorimetric method based on the blue color developed with thiocyanates and acetone was used. By using a calibration curve on a spectrophotometer, this method was made very rapid, and the results were correct within about 5 percent. The reagent used for developing the color contained 200 g of ammonium thiocyanate, 20 g of potassium pyrophosphate (for decolorizing iron compounds) and 50 ml of acetic acid, all dissolved in 500 ml of water and diluted with acetone to 1 liter.

Attempts were made to devise a colorimetric method for cobalt that would make use of the purple color developed in cobalt solutions by hydroxy acids. Such a method would permit the plating solutions to be analyzed directly, without the large dilutions required when sensitive colorimetric reagents are used. However, it was not found possible to secure reproducible colors, either on the acid or on the alkaline side. Ammoniacal cobalt solutions containing a hydroxy acid absorb oxygen and change color on standing.

The analysis of the nickel-tungsten solutions for nickel was simpler than the procedures required for cobalt. The nickel could be determined with the well known cyanide titration with sufficient accuracy, and the organic material did not interfere.

The total iron content of the iron-tungsten baths can be determined by any one of the standard methods, after the organic material is destroyed. No entirely satisfactory procedure has been worked out to determine both ferrous and ferric iron in a plating solution after it had been in operation. Colorimetric methods for either form of iron were not suitable, because in these dilute solutions the ferrous iron tended to oxidize. A reducing agent could not be added to stabilize the ferrous iron without danger of reducing some of the ferric iron. One method for determining ferrous iron is to titrate with permanganate after the sample has been acidified with acetic acid. The endpoint was not sharp, but higher acidities permitted oxidation of the organic acid. More accurate and rapid methods of analysis are needed.

The only hydroxy acid that was determined regularly was tartaric acid, which was done by oxidation with potassium permanganate, previously standardized with known amounts of tartrate.

V. Properties of Electrodeposited Tungsten Alloys

1. Criteria of Satisfactory Deposits

The properties of deposits that may be considered as commercially satisfactory may be summarized qualitatively as follows. The deposit should be mechanically sound, that is, a deposit not more than a tenth of a millimeter thick should hold together when the base metal is dissolved away, and under the microscope the deposit should not reveal any cracks or pores. Deposits up to a millimeter or more in thickness should be obtainable without many nodules. The deposits should not contain large amounts of inclusions, particularly oxides. The content of oxygen in ordinary electrodeposited chromium, that is, about 0.3 percent, may be considered an upper limit that can be present in deposits for engineering uses. Commercial electrodeposits of other metals contain less than 0.1 percent of oxygen. Of the many published processes for depositing metals or alloys few yield coatings useful for engineering applications. Studies on the electrodepositon of alloys have centered largely around the production and analysis of thin deposits and their variations with changes of plating conditions. No evidence has usually been offered to show whether the alloys are sound or whether thick deposits could be obtained.

The above criteria are met substantially by the cobalt-tungsten alloys and the nickel-tungsten alloys but not yet by the iron-tungsten alloys. The physical properties of the latter are inferior except in hardness, to the former two alloys. The iron-tungsten deposits are usually weak and brittle and may crack or fall apart when the base metal is dissolved.

2. Appearance of Tungsten Alloys

Deposits up to 0.1 mm thick are smooth and range in color from dark grey to bright. The cobalt-tungsten alloys have almost the same grey color as electrodeposited cobalt. The nickel alloys may vary from semibright to dark grey, the latter being obtained from the more concentrated tartrate plating solutions. The iron alloys vary from grey to bright, similar to chromium. The ap-

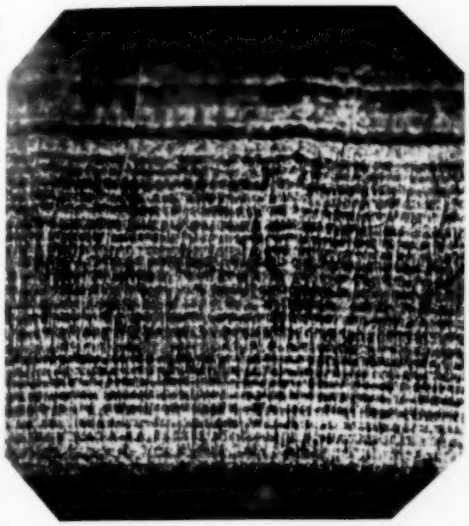

FIGURE 4. *Laminations in a cobalt-tungsten deposit, containing 23 percent of tungsten.*
X250.

pearance of the deposits may depend to some extent on the presence of small amounts of impurities in the bath.

3. Structure of Alloys

Microstructure.—As deposited, the alloys usually show laminations running parallel to the base metal, even though the current was not interrupted. In this respect the deposits resemble some "bright nickel" deposits. The iron alloys show this lamination to the greatest degree, and occasionally the adhesion is poor between the layers. Some of the cobalt-tungsten alloys show also a columnar structure perpendicular to the surface, similar to that of electrodeposited nickel or cobalt. Photomicrographs of a cobalt-tungsten and an iron-tungsten alloy deposit are shown in figures 4, 5, 6. When plated under unfavorable conditions, such as too high a current density, the alloy may contain voids and cracks. On heating above 1,000° C, the laminations disappear and a grain structure is developed (see fig. 7, 8).

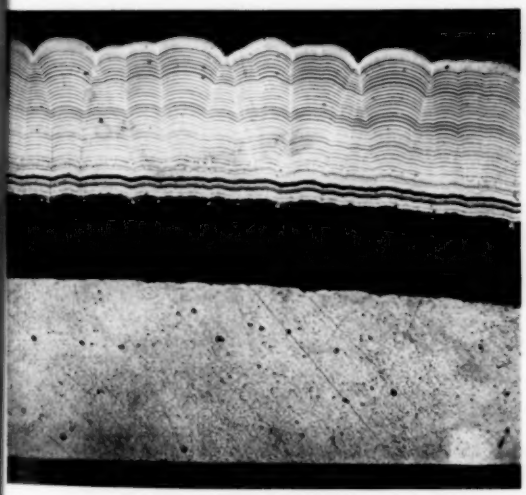

FIGURE 5. *Laminations in an iron-tungsten deposit, containing 48 percent of tungsten.*
X250.

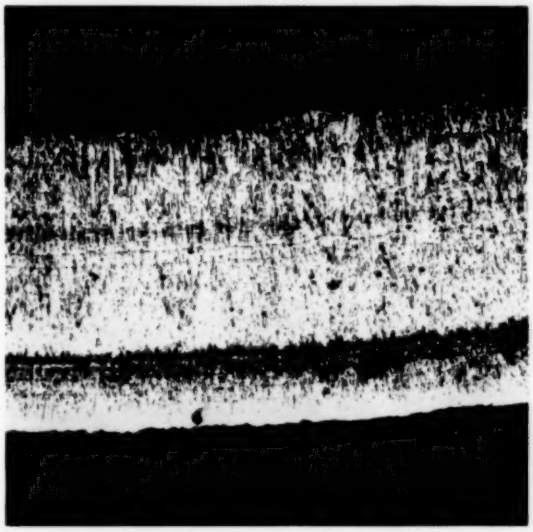

FIGURE 6. *Cobalt-tungsten alloy (25 percent tungsten) showing laminations parallel to the base metal and a columnar structure perpendicular to the base metal.*
X100.

Crystal Structure.—Previous X-ray studies of electrodeposited alloys have shown that they are generally composed of the same phases as those present in the comparable thermally prepared alloys. This was not borne out by X-ray studies of the electrodeposited cobalt-tungsten and iron-tungsten alloys. These appear to be solid solutions, although according to the equilibrium diagrams [10], a fair proportion of an intermetallic compound should be present as another phase. The importance of this structure will be discussed in connection with the precipitation-hardening of the alloys.

FIGURE 7. *Cobalt-tungsten alloy (also shown in fig. 6) after being heated to 1,300° C for 15 hr.*

Note disappearance of the laminations and the appearance of grains. X100.

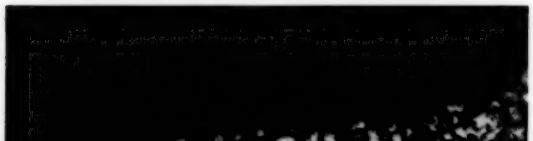

FIGURE 8. *Cobalt-tungsten alloy (also shown in figs. 6 and 7) after being precipitation-hardened at 800° C.*

The specimen has been overaged. X100.

4. Physical Properties

Hardness.—The hardness of the electrodeposited tungsten alloys is perhaps their most interesting property. Not only are they relatively hard as obtained from the bath, but they also increase in hardness when subjected to suitable heat-treatments, as shown in table 12. The hardness

TABLE 12.—*Hardness of electrodeposited tungsten alloys* [a]

No.	Type of bath	Tungsten in deposit	Vickers hardness		
			Initial	1 hr, 600° C	Change
	COBALT-TUNGSTEN				
		Percent			
1	Standard cobalt		330	250	−80
2	Gluconate	7	420	358	−62
3	do	2	341	284	−57
4	do	2	380	245	−135
5	do	4	348	294	−54
[b] 6	Tartrate	4	389	391	+2
7	Gluconate	4	426	459	33
8	do	5	452	555	103
9	Tartrate	8	461	467	6
10	Ammonium sulfate	9	425	413	−12
11	Tartrate	9	460	480	20
12	do	9	381	469	88
13	do	10	435	528	93
14	do	10	440	543	103
15	Gluconate	11	486	566	80
16	Tartrate	12	509	654	145
17	do	12	415	558	143
18	do	14	380	487	107
19	Malate	15	450	578	128
20	Tartrate	15	458	645	187
21	do	15	392	586	194
22	do	16	465	693	228
23	Malate	16	360	590	230
24	Tartrate	17	485	695	210
25	do	18	422	516	94
26	do	18	487	613	126
27	do	19	517	750	233
28	do	20	500	702	202
29	do	21	396	528	132
30	Hydroxyacetate	21	460		
31	Citrate	22	340	370	30
32	Tartrate	24	458	684	226
33	Malate	25	455	630	175
34	Tartrate	25	524	747	223
35	Hydroxyacetate	25	480		
36	Tartrate	26	704	988	284
37	do	31	470	757	287
38	do	33	615	810	195
39	do	35	684	824	140
40	do	36	535	710	175
41	Citrate	53	564	1,035	471
42	do	57	624	907	283

See footnotes at end of table.

TABLE 12.—*Hardness of electrodeposited tungsten alloys*—Continued

No.	Type of bath	Tungsten in deposit	Vickers hardness		
			Initial	1 hr, 600° C	Change
	NICKEL-TUNGSTEN				
		Percent			
1	Hydroxyacetate	1	513	258	−255
2	do	2	380	445	65
3	do	3	340	415	75
4	do	4	507	370	−137
5	Glycinate	5	345	268	−77
6	Hydroxyacetate	5	410	450	40
7	Tartrate	7	608	378	−230
8	Citrate	9	621	355	−266
9	Hydroxyacetate	10	370	420	50
10	Glycinate	11	600	600	0
11	Citrate	13	473	312	−161
12	do	14	508	867	359
[a] 13	Tartrate	14	498	344	−154
14	Citrate	17	591	744	153
15	do	25	662	783	121
16	do	25	532	379	−153
17	do	26	642	653	11
18	do	29	623	645	22
19	do	30	597	750	153
20	do	31	648	805	157
21	do	31	611	517	−94
22	do	33	643	772	129
23	do	36	693	752	59
	IRON-TUNGSTEN				
1	Citrate	48	960	1,200	240
2	do	49	720	920	200
3	do	51	890	1,400	510
4	do	52	750	1,350	600
5	do	52	960	1,120	160
[b] 6	do	53	1,010	1,400	390
7	do	53	1,340	1,020	−320
8	do	54	800	1,230	430
9	do	56	790	1,330	540
10	do	56	970	1,460	490
11	do	56	840	1,260	420

[a] Deposits having the same composition are not duplicates, but were plated from different solutions under different conditions.
[b] In this group, Nos. 6 to 42, the hardness increased as a result of heating.
[c] In this group, Nos. 13 to 23, the hardness increased as a result of heating.
[d] Plated at 70° C.

measurements were made either with an Eberbach microhardness tester, which uses a Vickers diamond, or with a Knoop tester, on a polished cross section of the coating, which was 0.05 mm or more in thickness. All hardness readings were converted to the Vickers scale.

The initial hardnesses of the cobalt and the nickel alloys were about the same, from 350 to 700 Vickers. On heating to 600° C for an hour and cooling, certain of these alloys increased in hardness by more than 100 points, probably as a result of precipitation hardening. The nickel alloys exhibited less tendency toward this increased hardening than did the cobalt alloys. The data in table 12 show that precipitation hardening occurred with cobalt-tungsten alloys containing above 5 percent of tungsten, and with nickel-tungsten alloys containing above 17 percent of tungsten. There are exceptions in both directions, however. Some alloys with a high tungsten content softened on heating and others with a low-tungsten content hardened. The increase in hardness on heating is variable and depends somewhat on the conditions of deposition as well as on the tungsten content.

The precipitation-hardening of the metallurgical nickel- and cobalt-tungsten alloys has been studied by Sykes and coworkers [11, 23, 24]. For precipitation-hardening to occur, the cobalt alloy had to contain more than 10 percent of tungsten and the nickel alloy more than 32 percent of tungsten. Precipitation-hardening occurs at lower tungsten contents with the electrodeposited alloys than with the metallurgical alloys. The maximum hardness obtainable for the metallurgical alloys by precipitation-hardening (about 500 Vickers) was less than that obtained with the electrodeposited alloys (about 700 Vickers).

The iron-tungsten alloys as deposited are considerably harder than the cobalt and nickel alloys. The hardness ranges from 700 to 900 Vickers, which is somewhat less than the hardness of bright chromium (about 900 to 1,000). After heating at 600° C for an hour the hardness of the iron alloy increases to from 900 to 1,400 Vickers. There seems to be no correlation of the hardness and the conditions of plating. If the hardness of the iron-tungsten alloy can be utilized commercially, there would be more incentive toward this development.

The effect of temperature and time of heating of the tungsten alloys on the precipitation-hardening was explored, but no thorough study was made. In figure 9 are shown the averages of the data for two cobalt-tungsten deposits. The optimum temperature for their hardening is 600° C. Higher temperatures and longer periods of heating at these temperatures cause a softening of the deposit, although the deposits are still quite hard (450 Vickers) after an hour at 1,200° C. A

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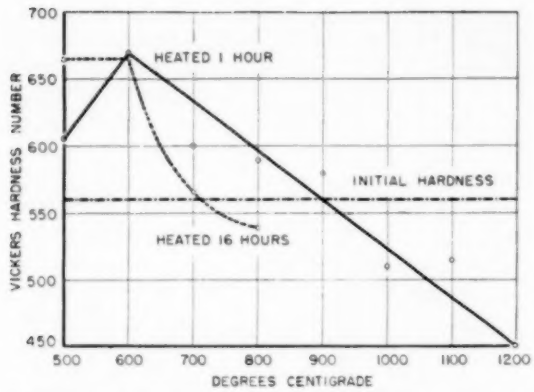

FIGURE 9. *Hardness of cobalt-tungsten alloys after being subjected to heat treatments.*

deposit containing about 25 percent of tungsten, which was heated at 1,300° C for 15 hours, decreased in hardness from 420 to 150 Vickers. This softened alloy was capable of being subsequently precipitation-hardened.

The optimum temperature of hardening for the nickel alloys appears to be below 600° C, because they become ductile at this temperature. The optimum temperature for the iron-tungsten alloys with 50 percent of tungsten seems to be above 600° C. The following results were obtained for an iron-tungsten deposit that had an initial hardness of about 780 Vickers. After heating for an hour at 600° C, the hardness was 780 Vickers; at 800° C, 1030 Vickers; and at 1,200° C, 990 Vickers.

The precipitation-hardening of these alloys differentiates them from other hard electrodeposits, such as hard nickel, which owe their hardness mainly to some type of internal stress. Hard nickel undergoes a stress relief at the comparatively low temperature of 300° C [27] and hence is not suitable for use at high temperatures.

The detection by X-rays of only a single-phase solid solution in the cobalt- and iron-tungsten alloys is of interest, because of its bearing upon the explanation of the hardening that takes place on heating. In the usual precipitation hardening of a thermally prepared alloy, it is heated to a temperature at which a solid solution is produced and is then cooled to room temperature with the solid solution still present but not completely in equilibrium. On holding the alloy at an elevated temperature (but below the initial high temperature), a second phase precipitates from the solid solution at the grain boundaries, and causes an increased hardness of the material. If the electrodeposited alloys were in an equilibrium condition, then the second phase (which may be either a solid solution or intermetallic compound) would already be present and there would be no tendency for it to deposit from the solid solution at the grain boundaries when the alloy is heated. However, the alloy is already in the form of a solid solution as deposited, that is, in a state comparable to the unstable thermal alloys. Hence precipitation-hardening readily takes place without the usual preliminary heat treatment. The close relation between the mechanism of the hardening of electrodeposited and the thermal cobalt-tungsten alloys is shown by the fact that the optimum temperature of hardening is about the same for both, viz 600° C.

This explanation of the hardening of the alloys does not suffice to explain the hardening of the nickel-tungsten alloys, as according to the phase diagram [10, 11], no second phase should precipitate if the content of tungsten is below 32 percent.

The formation of an intermetallic compound in the electrodeposited cobalt- and iron-tungsten alloys that had been hardened at 600° C could not be detected by X-rays. This does not necessarily mean that no compound has been formed, but rather, that the quantity is too small to be detected. On heating an iron-tungsten deposit to 1,200° C, new X-ray lines were obtained, which indicated the presence of a new phase that did not correspond very closely, however, with the lines reported for the iron-tungsten compounds, Fe_2W and Fe_3W_2.

Hot-Hardness.—The hot-hardness (that is, the hardness at elevated temperatures) of only the cobalt-tungsten alloys was measured (through the courtesy of the Climax Molybdenum Co.). The values are given in table 13, along with data on several other metals for comparison. The alloys with the higher tungsten contents show a good hot-hardness, comparable to that of stellite. Precipitation-hardening of the alloy (No. 8, table 13) increased its hot-hardness.

Ductility of the Alloys.—The ductility of the alloys was determined qualitatively by the permanent deformation obtained on bending a specimen. The iron alloys were brittle under all conditions of plating. The nickel and cobalt alloys had a slight ductility if they contained not over 5

percent of tungsten, otherwise they had no apparent ductility. On heating the nickel alloys to 600° C or above, and the cobalt alloys above 900° C, they become quite ductile. The temperature for this treatment of the cobalt alloys seemed rather critical, as no ductility was obtained at lower temperatures even after some hours of heating, whereas at the proper temperature for the alloy the ductility developed in a few minutes. This temperature varied somewhat with the composition of the alloy. Alloys containing up to 12 percent of tungsten could be made ductile by heating to 900° C, but the higher-tungsten alloys required a temperature of about 1,000° C. The temperatures required to produce ductility correspond approximately to the solid solubility line of Co_3W in the equilibrium diagram. The iron-tungsten alloys were still brittle after being heated to 1,200° C.

TABLE 13.—*Hot-hardness of cobalt-tungsten alloys and some other metals*

No	Metal	Vickers hardness number at—		
		20° C	700° C	800° C
1	Steel	290	50	36
2	Cobalt, electrodeposited	300	65	55
3	Cobalt-tungsten alloy, electrodeposited, 12% W	500	198	42
4	Cobalt-tungsten alloy, electrodeposited, 15% W	500	95	34
5	Cobalt-tungsten alloy, electrodeposited, 20% W	540	210	82
6	Cobalt-tungsten alloy, electrodeposited, 23% W [a]	510	150	53
7	Do [b]	560	160	64
8	Do [c]	610	300	180
9	Cobalt-tungsten alloy, electrodeposited, 25% W	520	370	220
10	Cobalt-tungsten alloy, cast, 7% W	340	195	110
11	Cobalt-tungsten alloy, cast, 12% W	510	220	105
12	Cobalt-tungsten alloy, cast, 15% W	.....	190	105
13	Cobalt-tungsten alloy, cast, 25% W	.....	.....	200
14	Stellite	470	300	.....
15	Do	315	200	175

[a] Alloy as deposited.
[b] Alloy heated to 1,000° C for 1 hr and 850° C for 1 hr.
[c] Alloy heated to 1,200° C for 1 hr. Precipitation hardened for 100 hr at 600° C.

Thermal Properties.—The dimensional changes on heating were determined only with the cobalt-tungsten alloys. Our interest in this measurement arose from the fact that when deposits 0.25 millimeter thick on steel were heated above 900° C to render them ductile, cracking would occasionally occur. To measure the dimensional changes that occurred on heating, a tubular specimen of the alloy, from which the base metal had been stripped, was heated and then cooled. The change in length of the tube as a result of the treatment was measured with a micrometer.

Dimensional changes as a result of heating seem to be characteristic of some electrodeposits. The contraction of chromium to the extent of about 1 percent when heated is well known Nickel deposited from strong chloride solution (unpublished work) shows permanent expansion of about 3 percent when heated The data in table 14 show that the cobalt-tungsten alloy may either expand or contract as a result of heating, and the effect does not seem to be highly reproducible As the expansions seem to occur chiefly with alloys that are plated from solutions with high concentrations of the organic constituent and of cobalt (1, 2, 11 to 14, table 14), they may be related to the presence of inclusions.

Coefficient of Thermal Expansion.—The coefficient of thermal expansion was measured at elevated temperatures to determine at what temperatures permanent dimensional changes occurred. The coefficient of thermal expansion of electrodeposited cobalt was measured as a basis of comparison. The specimens of alloy and cobalt used for these measurements were tubes about 30 cm long and 5 mm in diameter, which were obtained in the usual way by stripping out the copper tube on which the metal had been deposited. The data are shown in figure 10. The cobalt showed the presence of a transition point as 425° C, which has been reported previously for metallurgical cobalt [26]. The alloy specimens showed a fairly linear change in length with temperature until a temperature of about 800° C was reached, and from this point on, a rapid expansion in length was noted, the coefficient of expansion nearly quintupling during the next 150 degrees. On cooling, the original curve was not retraced, and at room temperature a permanent expansion was retained corresponding to the rapid expansion above 800° C. The average coefficient of thermal expansion for the range 0° to 900° C, as determined from the cooling curve, was 13.8×10^{-6} for the alloy, as compared with 14.5×10^{-6} for the electrodeposited cobalt.

Density.—The densities of the alloys were measured by the loss-in-weight method, using symmetrical tetrabromoethane as the liquid. Occasionally, the density of an alloy was measured as a means of rapidly determining its approximate composition. This can be done, because the

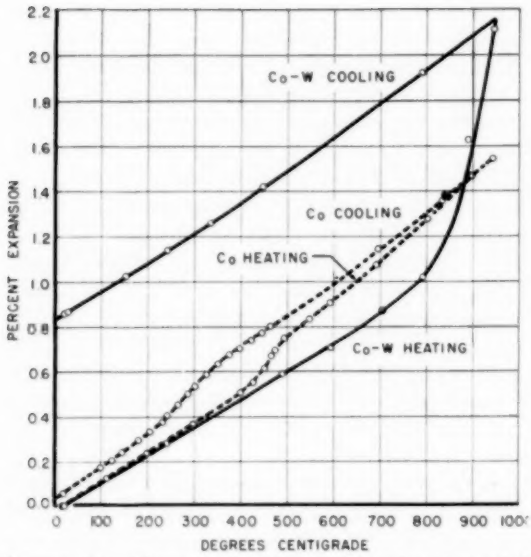

FIGURE 10.—*Thermal expansion of electrodeposited cobalt and cobalt-tungsten alloy, containing 10 percent of tungsten.*

Note the transition point at about 425° C shown by the curve for cobalt, and the increase in thermal expansion above 800° C shown by the curve for the cobalt-tungsten alloy.

densities of the iron group metals and of tungsten differ so widely. Figure 11 shows the calculated curve of percent tungsten with respect to density for the cobalt or nickel-tungsten alloys (assuming no volume change to have occurred in the formation of the alloy). The circles show the agreement obtained between the percent tungsten obtained by analysis and from the measurement of density. The agreement was usually about 1 percent, although occasionally larger errors occurred.

Mechanical Properties.—A few rough measurements of tensile strength were made of some nickel-tungsten alloys containing about 20 percent tungsten. The tensile strength varied from 78 kg/mm² to 110 kg/mm². These values may be low because in some tests specimens fractued at the grips. Electrodeposited cobalt was found to have a tensile strength of about 55 kg/mm².

Young's Modulus.—Young's modulus was determined by the flexure of a tube under load. Several results for Young's modulus are given in table 15. With the exception of one result for a nickel alloy that is low and may be the result of a defective specimen, the moduli for the three alloys

TABLE 14. *Change in length of tubes of electrodeposited cobalt-tungsten alloy after heating 1 hr at 1,000° C*

No.	Bath composition							Current density	Tungsten in deposit	Change in length
	Co		W		Organic salt					
	Molarity	g/liter	Molarity	g/liter	Type	Concentration				
						Molarity	g/liter			
TARTRATE SOLUTION										
								amp/dm²	*Percent*	*Percent*
1	1.7	100	0.14	25	Na, K	1.40	400	2	8	1.4
2	0.42	25	.03	5	Na, K	1.40	400	2	10	0.7
3	.42	25	.14	25	Na, K	0.70	200	2	20	−.3
4	.42	25	.14	25	Na, K	.70	200	5	27	−.2
5	.25	15	.08	15	Na, K	.35	100	2	14	1.5
6	.25	15	.08	15	Na, K	.35	100	5	22	−0.1
7[a]	.25	15	.08	15	Na, K	.35	100	2	24	−.2
8[a]	.25	15	.08	15	Na, K	.35	100	5	33	−.5
9	.10	6	.07	12	Na, K	.35	100	2		.0
10	.10	6	.07	12	Na, K	.35	100	5	28	.0
MALATE										
11	0.42	25	0.27	50	NH_4	0.0	500	5	9	2.5
12	.85	50	.27	50	NH_4	1.5	250	2	9	0.4
13	.85	50	.27	50	NH_4	1.5	250	5	14	.2
CITRATE										
14	0.60	35	0.03	5	NH_4	1.2	300	5	20	1.5

[a] Solution contained ammonium sulfate, 300 g/liter.

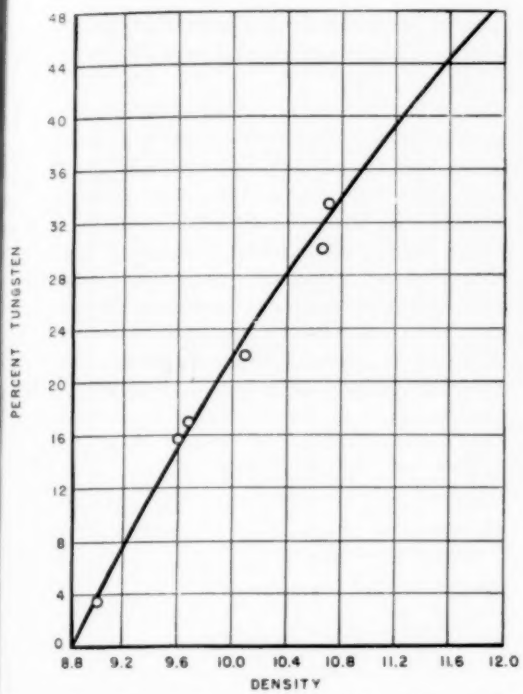

FIGURE 11.—*Percent of tungsten in cobalt-tungsten or nickel-tungsten alloys versus density.*

The circles indicate the composition of electrodeposited tungsten alloys as determined by analysis.

TABLE 15.—*YOUNG'S MODULUS OF ELECTRODEPOSITED TUNGSTEN ALLOYS*

No.	Iron group metal	Type of bath	Tungsten in deposit	Modulus	
			Percent	*lb/in.²×10⁶*	*kg/mm²×10³*
1	Co	Tartrate	15	24	17
2	Co	do	25	25	17
3	Ni	do	5	23	16
4	Ni	Hydroxyacetate	17	25	17
5	Ni	Inorganic	9	24	17
6	Ni	Tartrate	15	11	8
7	Fe	Citrate	46	25	17
8	Fe	do	49	23	16

seem to be about 17×10^3 kg/mm², which is lower than the modulus for the metals individually. (Moduli of the metals of the iron group are all about 21×10^3 kg/mm² and of tungsten, 36×10^3 kg/mm².

Fatigue Limit.—A few tests were run of the fatigue limit of a standard steel specimen plated with several thousandths of an inch of nickel- or cobalt-tungsten alloy. The steel used was X4130, which had a fatigue limit of 63 kg/mm². The alloys reduced the fatigue limit of the steel specimen to about 28 kg/mm², which is about the same result that is obtained with chromium coatings.

Frictional Properties.—No quantitative measurements of the coefficient of friction were made. However, in some qualitative experiments on galling in which the dry surfaces were rotated in contact under light loads, the cobalt-tungsten alloy behaved particularly well. This alloy has also been plated on small pivots and bearings, such as are used in instruments. Incomplete tests indicate that the performance of the alloy was satisfactory but not equal to that of jeweled bearings.

Electrical Properties.—The resistivities of cobalt-tungsten alloys of various compositions are given in table 16. The resistivity varies almost linearly with the percentage of tungsten in the deposit (see fig. 12). Even after annealing, the resistivity of cobalt and of the tungsten alloys is still much

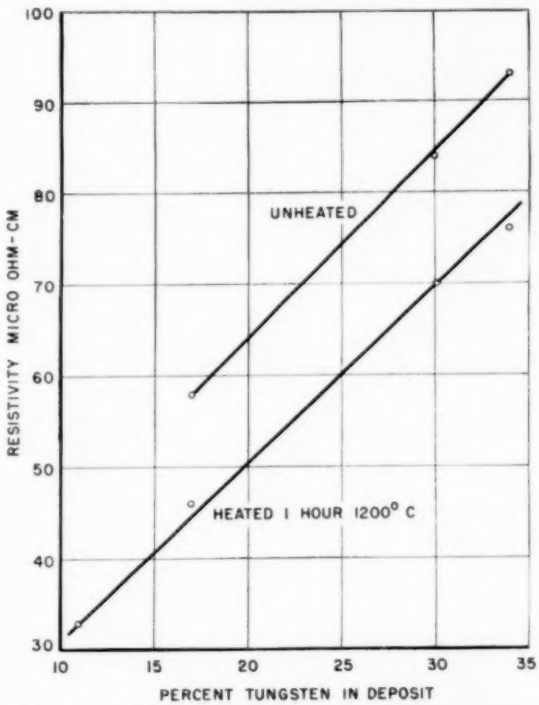

FIGURE 12.—*Resistivity of electrodeposited cobalt-tungsten alloys versus percent of tungsten.*

The resistivity is a linear function of the percentage of tungsten.

TABLE 16.—*Electrical resistivity of electrodeposited tungsten alloys*

[Each solution contained Rochelle salt, 400 g/liter and ammonium chloride, 50 g/liter. Solutions were operated at 90° C, with a pH of 8.5 to 9.0 and a current density of 2 amp/dm².]

No.	Co		W		Tungsten in deposit	Resistivity—	
	Molarity	g/liter	Molarity	g/liter		As deposited	Heated 1 hr at 1,200° C
					Percent	*Microhm-cm*	*Microhm-cm*
1 [a]	5.1	120				10	
2	0.42	25	0.03	5	11.4		[b] 33
3	.40	23	.04	7	17	58	46.5
4	.20	12	.54	100	29.7	84	69.5
5	.51	30	.30	56	33.4	93	76.7

[a] Cobalt plating bath, pH 4; no tungsten. [b] Heated 1 hour at 1,000° C.

higher than that of the individual metallurgical metals. (Tungsten, 5.1; and cobalt 9.7 microhm-cm.)

Magnetic Properties.—Most of the nickel-tungsten alloys containing above 20 percent of tungsten are not ferromagnetic. The dividing line is not sharp, and the plating conditions also have an effect on the magnetic properties of the alloys. The cobalt-tungsten alloys containing up to 30 percent of tungsten were magnetic. The iron-tungsten alloys were not consistent in magnetic behavior. Of those containing about 50 percent of tungsten, the majority were magnetic, but some were nonmagnetic, although they had been similarly plated.

TABLE 17.—*Oxygen and hydrogen content of electrodeposited tungsten alloys*

No.	Metal	Metal concentration		W		Salt			Current density	Temperature	Composition of deposit		
						Type	Concentration				Tungsten	Hydrogen	Oxygen
		Molarity	g/liter	Molarity	g/liter		Molarity	g/liter					
	INORGANIC												
									amp/dm²	*°C*	*Percent*	*Percent*	*Percent*
1	Cobalt	2.10	125						2	25		0.004	0.949
	TARTRATE												
2	Cobalt	0.42	25	0.03	5	Na, K	1.40	400	2	90	14	0.011	0.98
3	do	.42	25	.03	5	Na, K	1.40	400	2	25	22	.064	1.14
4	do	.42	25	.03	5	Na, K	1.40	400	5	90	18	.014	0.16
5	do	.42	25	.14	25	Na, K	1.40	400	2	90	25	.008	.07
6	do	.42	25	.27	50	NH_4	2.00	370	2	90	23	.009	.08
	CITRATE												
7	Cobalt	0.42	25	0.07	13	Na	0.60	200	2	90	42	0.027	0.43
8	do	.42	25	.03	5	NH_4	1.20	300	2	90	20	.012	.17
	INORGANIC												
9	Nickel	0.95	55						2	25		0.002	0.09
	TARTRATE												
10	Nickel	0.68	40	0.20	35	Na, K	0.70	200	2	90	5	0.004	0.05
10A	do	.68	40	.20	35	Na, K	.70	200	2	25	13	.042	.38
	INORGANIC												
11	Iron	2.0	110						10	95		.001	.02
	CITRATE												
12	Iron	0.45	25	0.14	25	NH_4	0.41	100	3	90	49	0.002	0.04

Reflectivity.—The specular reflectivity of polished nickel-tungsten alloys was found to range from 58 percent to 61 percent, which is close to that of nickel (60 percent).

5. Chemical Properties

Oxygen Content of the Alloys.—The oxygen content of electrodeposited metals is of importance, as a high oxygen content indicates that much basic matter is being included in the deposit. Deposits with a high-oxygen content usually have inferior physical properties, such as brittleness and low strength. Table 17 shows some results for tungsten alloys along with cobalt and nickel for comparison. The oxygen content of the alloys is slightly higher than that of the iron group metals deposited separately.

From table 17 it is seen that Co-W deposits from citrate solutions have a higher oxygen content than those from tartrate solutions (compare 7 and 8 with 2 and 6); and deposits from solutions made up with ammonium salts of the organic acids have a lower oxygen content than from those containing the sodium salts (compare 5 and 6; and 7 and 8). Deposits plated at room temperature have a large content of oxide inclusions (No. 3 and 10A), which explains why they are so unsound.

The hydrogen content of the deposits ranges from 1 to 3 times the amount necessary to combine with the oxygen as OH groups.

Carbon Content.—When hardening of these alloys on heating was first observed, it was believed to be caused by the formation of tungsten carbide from the carbon that might be included in the deposits. It was known that some bright nickel deposits which are plated from solutions containing organic addition agents contain several tenths of a percent of carbon [21]. The analyses of some typical nickel- and cobalt-tungsten alloys showed that the deposits contained less than 0.01 percent of carbon, and therefore the hardening could not have been caused by the presence of carbon.

Attack of Cobalt- and Nickel-Tungsten Alloys by Reagents.—The attack of nickel- and cobalt-tungsten alloys by hydrochloric, nitric, sulfuric, and acetic acids, and by solutions of ammonium chloride and ammonium hydroxide was compared with the action of these reagents on the unalloyed electrodeposited metals. The cobalt alloys behaved very similarly to electrodeposited cobalt, and the nickel alloys showed slightly less attack than electrodeposited nickel. The data are shown in table 18, which contains the average results for alloys of three different compositions. On the basis of the chemical inertness of tungsten a greater resistance to chemical attack was expected of the alloys. The resistance of the alloys to solution by nitric acid seems to be the chief difference from the electrodeposited cobalt and nickel.

TABLE 18. *Attack of cobalt- and nickel-tungsten alloys by chemical reagents*

Reagent	Loss in weight, mg/cm² per day			
	Cobalt	Cobalt-tungsten (10 to 30% W)	Nickel	Nickel-tungsten (5 to 25% W)
Ammonium chloride, 200 g/liter.	0.25	0.4	0.3	0.25
Ammonium hydroxide, conc.	.25	.25	.15	.2
Hydrochloric acid, 1:1	.65	.9	.85	.3
Sulfuric acid, 1:1	.0	.25	.0	1.1
Acetic acid, 1:1	1.1	1.25	1.65	0.5

Reagent	Loss in weight, mg/cm² per hr.						
	Cobalt [a]	Cobalt tungsten [b]			Nickel [b]	Nickel-tungsten	
		10% W	35% W	41% W		5% W	23% W
Nitric acid, 1:1	1,200	13	4	1	16	1	1

[a] Based on 10-min test. [b] Based on 4-hr test.

6. Protective Value of Alloy Coatings on Steel

Flat steel panels, plated with cobalt-tungsten and nickel-tungsten alloys of three different compositions were subjected to the salt spray for 5 days, along with similar panels plated with nickel and cobalt alone. The coatings had the following thicknesses: 0.006, 0.013, and 0.025 mm (0.00025, 0.0005, and 0.001 in.). The cobalt and cobalt-tungsten alloy panels (see fig. 13) showed superior protective value to nickel or nickel-tungsten alloys (see fig. 14), the cobalt alloy coatings being the better. The break-down of the panels in all cases resulted from the porosity of the coatings. The nickel coatings showed the usual degree of porosity, which varied from a liberal sprinkling of a hundred or more spots per square decimeter on the thin coating to several pores per square decimeter on the thicker coatings. The behavior of the thin cobalt-tungsten alloy coatings

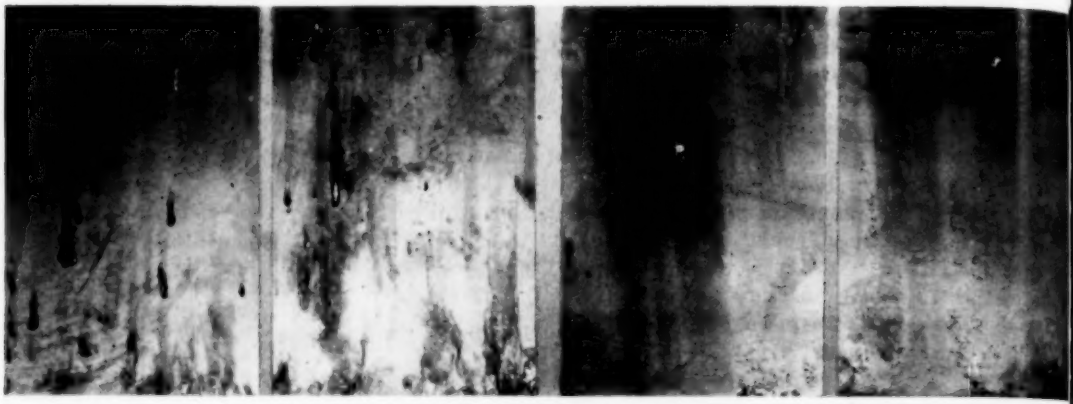

FIGURE 13. *Appearance of steel panels, plated with cobalt and with cobalt-tungsten alloy (20 percent tungsten), after exposure of 5 days to the 20-percent salt-spray test.*

The first two (left) are plated with cobalt and the last two (right) with alloy. Thickness of coatings, first and third: 0.006 mm (0.00025 in.); second and fourth, 0.025 mm (0.001 in.).

was outstanding; after 5 days of exposure to the salt spray, they did not develop more than a few pores and were in much better condition than the thick coatings of nickel (see fig. 13).

7. Field of Application of Tungsten Alloys

The tungsten alloys should find applications where hardness, particularly at elevated temperatures, is required. They may be competitive with chromium and hard nickel for building up worn parts or for use in dies. The good throwing power of these alkaline plating solutions should make the plating of many objects with tungsten alloy much simpler than with chromium, as complicated anodes would not be required. Suggested fields of application are on bearings, tool pistons, cylinders, and dies.

The main disadvantage involved in the plati of these alloys is that the operating conditio require elevated temperatures, and contin addition of ammonia to maintain the pH necessary.

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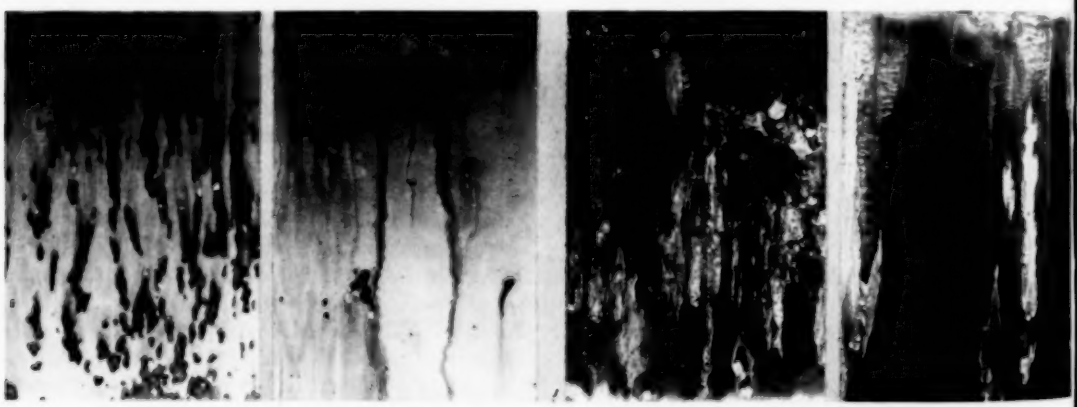

FIGURE 14. *Appearance of steel panels, plated with nickel and with nickel-tungsten alloy (15 percent tungsten), af an exposure of 5 days to the 20-percent salt-spray test.*

The first two (left) are plated with nickel and the last two (right) with alloy. Thickness of coatings, first and third: 0.006 mm (0.00025 in.); second an fourth, 0.025 mm (0.001 in.).

ent of some of the properties of the alloys, rticularly H. E. Cleaves for the measurements the oxygen and hydrogen content, to William Roeser for measurements of hardness, to H. C. acher for X-ray examination, and to Peter idnert for coefficient of thermal expansion. he authors acknowledge the assistance of A. F. sborn of the Geophysical Laboratory, who amined the alloy deposits in the earlier stages the work.

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